

## REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information. Send collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE November 8, 1999	3. REPORT TYPE AND DATES COVERED Final Report, 9/30/96 - 9/29/99	
4. TITLE AND SUBTITLE Elastomeric Phases for Toughening Air Force High-Temperature Polymers			5. FUNDING NUMBERS G F49620-96-10235	
6. AUTHOR(S) C. Kumudine, J.K. Premachandra, J.E. Mark M.R. Unroe, and F.E. Arnold				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemsitry University of Cincinnati Cincinnati, OH 45221-0172			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NI ATTN: AASERT Program 110 Duncan Ave., Room B115 Bolling Air Force Base, DC 20332-8050			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES None				
12a. DISTRIBUTION STATEMENT A Approved for Public Release Distribution Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A number of high-temperature polymers of interest and importance to the U.S. Air Force have a degree of brittleness that limits their utilization. This brittleness was reduced, and a number of other physical properties were improved, by the in-situ introduction of dispersed elastomeric phases. This was done in a modification of the sol-gel approach previously used to modify other properties by the introduction of much harder ceramic-like phases.				
14. SUBJECT TERMS High-temperature polymers, toughening, silica-siloxane phases, mechanical properties			15. NUMBER OF PAGES 55	
17. SECURITY CLASSIFICATION OF REPORT Unclassified			16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified		20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)  
Prescribed by ANSI Std. Z39-18  
298-102

DTIC QUALITY INSPECTED 3

19991215 077

53-85

**SUMMARY OF RESEARCH**  
**AASERT Supplement F49620-96-10253 to**  
**AFOSR Grant F49620-96-10052**

**“Elastomeric Phases for Toughening Air Force High-Temperature Polymers”**

Some high-temperature polymers, specifically two poly(arylene ether)s and a hydroxypoly(benzoxazole) (HPBO) copolymer, were toughened using dispersed rubbery phases generated by the sol-gel process. These rubbery phases were introduced using combinations of sol-gel precursors with varying numbers of alkyl groups. The sol-gel precursors used for this purpose were tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMOS) and dimethyldimethoxysilane (DMDMOS). The optimal molar ratio of the sol-gel precursors which gave the desired properties was used to prepare samples with varying amounts of the dispersed phase. In the case of HPBO polymer, the bonding agent, isocyanatopropyltriethoxy silane was used to facilitate the bonding between the two phases. The resulting samples were characterized with regard to their transparency, morphology, mechanical and thermal properties, and the extent of water absorption.

A good dispersion of the rubbery second phase was demonstrated by the clarity of the resulting samples. In addition, the scanning electron micrographs showed uniformly dispersed particles in these composite materials. In poly(arylene ether)s, a significant increase in toughness and ultimate elongation were achieved for samples prepared from relatively large amounts of sol-gel precursor with larger numbers of alkyl groups. In HPBO samples having low levels of the rubbery phase, both toughness and ultimate elongation were increased with increasing amount of the rubbery phase. Improvements in these properties of the HPBO polymer are rather large compared to the poly(arylene ether) polymers. The results also demonstrated improved thermal properties and decreased water absorption.

Details of this work are given in an article published in the Materials Research proceedings book *Organic/Inorganic Hybrid Materials*, and in a manuscript submitted for publication in the journal *Polymer*. Copies of both are attached.

In addition, high-temperature sulfopoly(benzobisthiazole)-silica aerogels were prepared using the sol-gel process followed by supercritical drying. Morphologies of the samples were investigated using small angle x-ray scattering,  $N_2$  absorption measurements, and transmission electron microscopy. The values of Young's modulus obtained from the initial slopes of the compression stress-strain curves decreased with increase in the amount of polymer present in the aerogels. According to the stress-strain results in compression, the deformabilities of the silica aerogels were significantly increased by incorporation of the organic polymer into the inorganic silica network. These hybrid aerogels are thus much less brittle. In addition, values of Poisson's ratio for some samples were used to estimate longitudinal sound velocities, which can be important in some applications of aerogel materials in general. Details are given in the attached article from the *Journal of Macromolecular Science: Pure and Applied Chemistry*.

# DEVELOPMENT OF SOME PROMISING APPROACHES FOR THE TOUGHENING OF HIGH-TEMPERATURE POLYMERS

C. KUMUDINIE<sup>1</sup>, J. K. PREMACHANDRA<sup>1</sup>, J. E. MARK<sup>1</sup>, T. D. DANG<sup>2</sup>, M. R. UNROE<sup>2</sup>, AND F. E. ARNOLD<sup>2</sup>

<sup>1</sup>Department of Chemistry and the Polymer Research Center, University of Cincinnati, Cincinnati, OH 45221-0172

<sup>2</sup>Polymer Branch, Air Force Research Laboratory, AFRL/MLBP B654, Wright-Patterson Air Force Base, OH 45433-7750

## ABSTRACT

High-temperature poly(arylene ether) and hydroxypolybenzoxazole polymers were toughened using dispersed rubbery phases. This rubbery phase was a hybrid material which was in-situ generated within the polymer matrix using mixtures of partially-hydrolyzable trialkoxy and dialkoxo organosilanes with a fully hydrolyzable tetraalkoxysilane. The resulting materials were characterized with regard to their structures, mechanical properties (modulus, ultimate strength, maximum extensibility, and toughness), thermal properties, optical properties, and tendencies to absorb water. Some of the results are presented here.

## INTRODUCTION

The sol-gel process has been widely used to prepare organic-inorganic hybrid materials providing desired properties from both organic and inorganic components. This technique is based on the in-situ generation of ceramic phases within the organic polymer by the hydrolysis of an organometallic compound [1,2]. Polymeric composites involving high-temperature polymers have been prepared [3,4], in some cases with proper bonding between the organic and inorganic phases through the use of a bonding agent [5]. In such cases, polymers with specific functional groups or functionalized copolymers were employed [5].

High-temperature resistant polymers find a wide range of applications in the aerospace industry, which is increasingly demanding polymer composites to meet more stringent requirements for use in advanced aircraft and aerospace vehicles.

Polycarbonate and polymethylmethacrylate thermoplastic polymers already provide excellent transparency and impact properties for current military aircraft canopies, windows and windcreens [6]. However, the use of these materials at very high temperatures is impossible because of their low thermal stabilities. For this reason, many polymeric compositions with higher use temperature backbones have been prepared and evaluated for window applications [6].

Most high-temperature polymers contain aromatic or heteroaromatic units. These rigid units tend to make the polymers brittle. Therefore, the polymers need to be toughened for applications in advanced structural composites and other neat-resin applications including canopies. The technique of toughening a brittle polymer by introducing a rubbery phase has been known for more than two decades. Various types of elastomers have been employed for rubbery phases providing toughening effects in both the thermoplastics and thermosets [7-9]. Diene polymers such as natural rubber, and copolymers [10] involving monomers such as butadiene are frequently used for this purpose. Their unsaturated structures can be an advantage with regard to reactions providing bonding between the phases, but also cause losses in stability especially at high temperatures. Therefore, there is considerable interest in using totally-saturated elastomers.

In the present study, high-temperature polymers, poly(arylene ether) (6F-ETPP-E) and hydroxypolybenzoxazole copolymer (HPBO) were toughened. 6F-ETPP-E polymer has been evaluated as a potential transparency material [6] and the repeat unit of the HPBO copolymer has an OH functional group which can be used to make a bond between the polymer and the rubbery phase by the use of a bonding agent.

The second phase was generated using the sol-gel process. In contrast to the reinforcing of polymeric materials using silica generated in-situ by the sol-gel technique, the current

approach employs the same technique to toughen brittle polymeric materials. For this purpose, trialkoxy organosilanes  $R^1Si(OR^2)_3$  and/or even dialkoxysilanes  $R^1R^2Si(OR^2)_2$  were added to the tetraalkoxysilanes. Their hydrolyses and condensations yield products containing non-hydrolyzable  $R^1$  and  $R^2$  groups, which give the generated phases the deformability associated with the toughness [11].

The resulting materials were characterized with regard to their structures, mechanical properties (modulus, ultimate strength, maximum extensibility, and toughness), thermal properties, optical properties, and tendencies to absorb water. Some of the results are presented here.

## EXPERIMENT

### Polymers and Reagents

The polymers 6F-ETPP-E and HPBO (Fig. 1) were prepared at the Wright-Patterson Air Force Base. The organosilanes tetramethoxysilane (TMOS) (99+%), methyltrimethoxysilane (MTMOS) (99+%), and dimethyldimethoxysilane (DMDMOS) (99+%) were purchased from United Chemical Technologies Inc. Tetrahydrofuran (THF) (anhydrous) was purchased from Aldrich Chemical Company, and diethylamine was purchased from Fisher, Inc. The bonding agent, isocyanatopropyltriethoxysilane (95%) for the HPBO polymer was purchased from United Chemical Technologies, Inc.

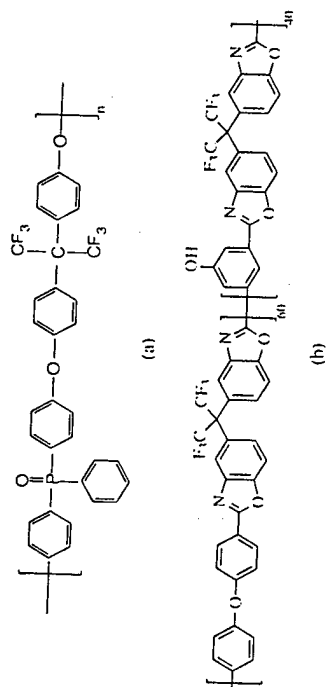


Fig. 1. High-temperature polymers being toughened: (a) 6F-ETPP-E and (b) HPBO.

### Preparation of the Composites

The desired amounts of polymers were dissolved in anhydrous THF. In the case of HPBO, the bonding agent isocyanatopropyltriethoxysilane was added in stoichiometric amounts relative to the OH groups in the copolymer. After clear solutions were obtained, the desired amounts of TMOS and MTMOS and/or DMDMOS were added. The mixture was stirred at room temperature to again give a clear solution. Then stoichiometric amounts of distilled water containing 5 wt% diethylamine were then added. The mixture was further stirred at room temperature to permit further hydrolysis and condensation and finally was transferred to Petri dishes and dried slowly in air. The resulting films were further dried under vacuum at 60 °C for 2 days.

Optimizing the properties concerned involved two steps. In the first, the amounts of TMOS and DMDMOS and/or MTMOS were varied to obtain optimum properties for a selected

percent rubbery phase, e.g., 10 wt%. A series of samples varying in the TMOS:DMDMOS mole ratio, 3:1, 2:1, 1:1, 1:2, and 1:3, were thus prepared. In the second step, this optimal mole ratio of TMOS and DMDMOS and/or MTMOS was used to prepare a series of samples having different amounts of the rubbery phase.

### Characterization of the samples

The samples were characterized with regard to their mechanical and thermal properties, water absorption, transparency and morphology.

Moduli, ultimate strengths, and maximum extensibilities were measured at room temperature using an Instron mechanical tester. Samples with dimensions approximately 50 x 5 x 0.2 mm<sup>3</sup> were tested at a cross-head speed of 0.1 in/min.

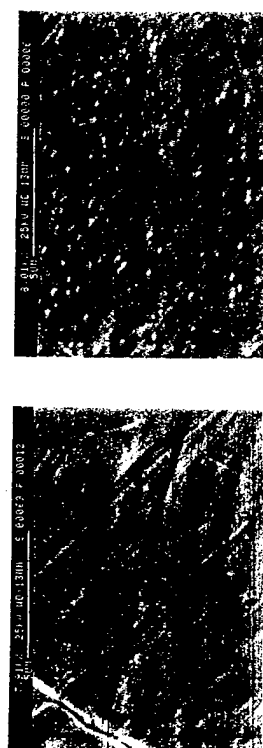
Scanning Electron Microscopy (SEM) was used to characterize both the film surfaces and their cross sections.

The extents of water absorption of these materials were investigated using the method described in ASTM-D570-81.

## RESULTS AND DISCUSSION

### Morphology

In most cases, the samples were transparent indicating good dispersion of the second rubbery phase. The SEM results of the unfractionated surfaces of the pure 6F-ETPP-E polymer and the sample having 10 wt% rubbery phase with 1:1 TMOS:DMDMOS mole ratio are shown in Fig. 2 (a) and 2 (b) respectively. Fig. 2 (b) shows uniformly distributed rubbery particles in the hybrid material.



(a)

(b)

Fig. 2. The SEM results for the unfractionated surfaces of (a) the pure polymer and (b) the sample with 10 wt% rubbery phase having a 1:1 TMOS:DMDMOS mole ratio.

### Mechanical Properties

In the case of 6F-ETPP-E, the modulus of the sample having 3:1 of TMOS:DMDMOS mole ratio has been increased and those having 1:2 and 1:3 mole ratios have been decreased, compared to that of the pure polymer (Fig. 3 and Table 1). (For all the samples of 6F-ETPP-E and HPBO tested, the moduli had uncertainty values less than 4.5%.) There is no noticeable change in moduli of the samples having 2:1 and 1:1 mole ratios of TMOS:DMDMOS. The

ultimate strengths of the samples with rubbery phase have been decreased compared to the pure polymer except for the sample with 1:2 mol ratio of TMOS:DMDMOS. The values of toughness (area under the stress-strain curve) were increased for all the samples except for samples having 3:1 and 2:1 mole ratios of TMOS:DMDMOS. This decrease in the toughness for the samples corresponding to higher amounts of TMOS could have been anticipated, since the amounts of glassy silica were higher in those samples. The increase in toughness and the decrease in the moduli for the samples having 1:2 and 1:3 of TMOS:DMDMOS mole ratios is presumably due to the silica particles being modified by incorporating organic groups which provide the rubbery properties. More than two fold increases in toughness were achieved for samples with 1:1 and 1:3 of TMOS:DMDMOS mole ratios.

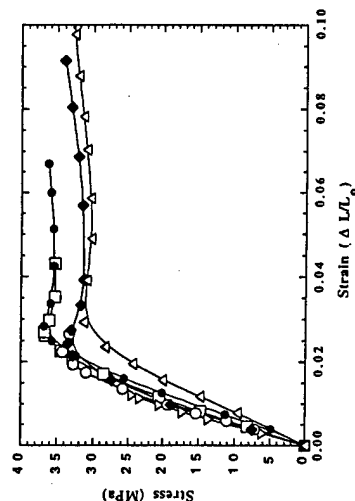


Fig. 3. Stress strain curves for 6F-ETPP-E pure polymer (□), and for samples containing 10 wt% rubbery phase with 3:1 (▽), 2:1 (○), 1:1 (◆), 1:2 (●), and 1:3 (Δ) TMOS:DMDMOS mole ratios.

Table 1. Mechanical properties of the 6F-ETPP-E composites

Rubbery phase wt%	Sol-gel precursor*	Modulus (MPa)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
0	—	1820	35.3	4.3	1.17
10	TMOS:DMDMOS (3:1)	2060	24.4	1.2	0.18
10	TMOS:DMDMOS (2:1)	1940	33.4	2.7	0.59
10	TMOS:DMDMOS (1:1)	1940	34.0	9.4	2.69
10	TMOS:DMDMOS (1:2)	1580	36.3	6.7	2.05
10	TMOS:DMDMOS (1:3)	1370	32.8	10.4	2.81

\*Molar ratios of the corresponding precursors are given in parenthesis

Fig. 4 and Table 2 show the mechanical properties of the HPBO pure polymer and the samples containing varying amounts of the rubbery phase with a 1:1 TMOS:MTMOS mole ratio. Incorporation of the rubbery phase into the polymer has increased the ultimate elongation and toughness without causing any significant change in modulus, except for the sample having 20 wt% rubbery phase. The decrease in ultimate elongation and toughness of the sample with 20 wt% rubbery phase may be due to possible phase separation when large amounts of the second phase are introduced. The ultimate strengths of these materials do not show any obvious trend with increase in the amount of rubbery phase. By incorporating a small amount of the rubbery

phase (e. g. 5 wt%), the ultimate elongation and the toughness were increased to a large extent; however, further incorporation of the rubbery phase did not increase the ultimate elongation in the same proportion. Improvements in ultimate elongation and toughness of the HPBO polymer are rather large compared to that of the 6F-ETPP-E polymer. This may be due to the interfacial bonding between the phases being improved by the use of the bonding agent in the case of the HPBO polymer.

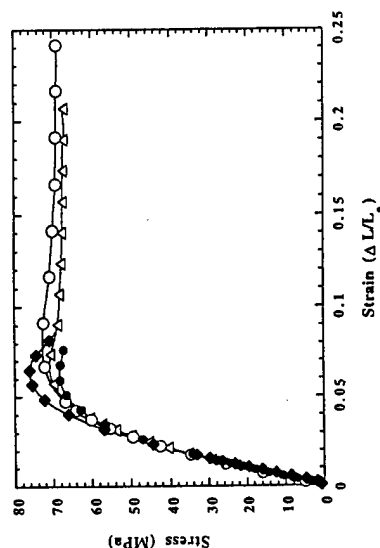


Fig. 4. Stress-strain curves for HPBO pure polymer (◆), and for samples containing 1:1 of TMOS:MTMOS mole ratio: 5 (Δ), 15 (○), and 20 (●) wt% rubbery phase.

Table 2. Mechanical properties of the HPBO composites

Rubbery phase wt%	Sol-gel precursor	Modulus (MPa)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
0	—	2140	69.1	8.9	4.95
5	TMOS:MTMOS (1:1)	2040	66.7	20.9	12.8
15	TMOS:MTMOS (1:1)	2120	68.7	24.3	15.8
20	TMOS:MTMOS (1:1)	2050	67.0	7.6	3.84
5	TMOS:DMDMOS:	2100	67.0	13.3	8.08
15	TMOS:DMDMOS:	1980	63.9	14.3	9.28
20	TMOS:DMDMOS:	2070	63.9	11.9	6.37
	MTMOS (1:1:1)				

Fig. 5 shows stress-strain curves for some HPBO samples with varying amounts of the second phase, which was generated using all three sol-gel precursors in 1:1:1 mole ratio. The mechanical properties are summarized in Table 2. In this case as well, the moduli of all three samples having different amounts of rubbery phase were almost the same as that of the pure HPBO polymer. However, in this case, the improvements in ultimate elongation and toughness are smaller compared to the previous case with the rubbery phase generated using a 1:1 mole ratio of TMOS:MTMOS.

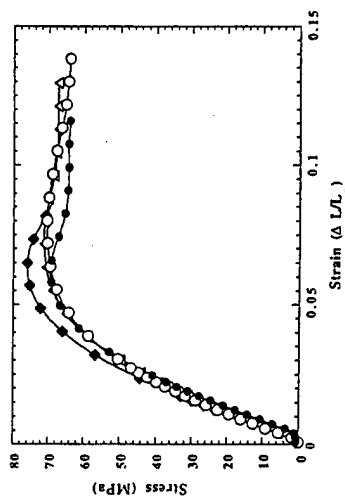


Fig. 5. Stress-strain curves for HPBO pure polymer ( $\blacklozenge$ ), and for samples containing 1:1 of TMOS:DMDMOS:MTMOS mole ratio: 5 ( $\Delta$ ), 15 ( $\circ$ ), and 20 ( $\bullet$ ) wt% rubbery phase.

#### ACKNOWLEDGMENT

It is a pleasure to acknowledge the financial support provided by the Air Force Office of Scientific Research (Directorate of Chemistry and Materials Science) through Grants F49620-96-1-0052 and F49620-96-1-0235.

#### REFERENCES

1. C. J. Brinker and G. W. Scherer, *Sol-Gel Science* (Academic Press, New York, 1990).
2. J. E. Mark, C. Y.-C. Lee, and P. A. Bianconi, Eds., *Hybrid Organic-Inorganic Composites*, vol. 585 (American Chemical Society, Washington, 1995).
3. J. E. Mark, S. Wang, and Z. Ahmad, *Macromol. Symp.* **98**, 731 (1995).
4. Z. Ahmad, S. Wang, and J. E. Mark, in *Better Ceramics Through Chemistry VI*, A. Cheetham, C. J. Brinker, M. L. McCartney, and C. Sanchez, Eds. (Materials Research Society, Pittsburgh, 1994), vol. 346, p. 127.
5. J. Premachandra, C. Kumudinie, W. Zhao, J. E. Mark, T. D. Dang, J. P. Chen, and F. E. Arnold, *J. Sol-Gel Sci. Technol.* **7**, 163 (1996).
6. M. R. Unroe, R. K. Gupta, R. B. Sharma, and N. C. Thiesing, *Polym. Preprints, ACS, Div. Polym. Chem.* **38** (2), 293 (1997) and references cited therein.
7. C. K. Riew, Ed., *Rubber-Toughened Plastics* (American Chemical Society, Washington, DC, 1989), vol. 222.
8. C. K. Riew and A. J. Kinloch, Eds., *Toughened Plastics I* (American Chemical Society, Washington, DC, 1993), vol. 233.
9. A. A. Collyer, Ed., *Rubber-Toughened Engineering Plastics* (Chapman & Hall, Washington, DC, 1994).
10. M. Ishikawa, *Polymer* **36**, 2203 (1995).
11. Y.-P. Ning and J. E. Mark, *Polym. Bulletin* **12**, 407 (1984).

**MATERIALS RESEARCH SOCIETY  
SYMPOSIUM PROCEEDINGS VOLUME 519**

# **Organic/Inorganic Hybrid Materials**

Symposium held April 13-17, 1998, San Francisco, California, U.S.A.

## **EDITORS:**

**Richard M. Laine**  
*University of Michigan  
Ann Arbor, Michigan, U.S.A.*

**Clément Sanchez**  
*Université Pierre et Marie Curie  
Paris, France*

**C. Jeffrey Brinker**  
*Sandia National Laboratories  
Albuquerque, New Mexico, U.S.A.*

**Emmanuel Giannelis**  
*Cornell University  
Ithaca, New York, U.S.A.*



**Materials Research Society**  
*Warrendale, Pennsylvania*



# **Toughening of some high-temperature poly(arylene ether)s and a hydroxypoly(benzoxazole) by sol-gel generated rubbery particles**

**Chandima Kumudinie, Jagath K. Premachandra and  
James E. Mark\***

*Department of Chemistry and the Polymer Research Center  
The University of Cincinnati, Cincinnati, OH 45221-0172*

**Thuy D. Dang, Marilyn R. Unroe and Fred E. Arnold**

*Polymer Branch, Air Force Research Laboratory, AFRL/MLBP B654  
Wright-Patterson Air Force Base, OH 45433-7750*

Some high-temperature polymers, specifically two poly(arylene ether)s and a hydroxypoly(benzoxazole) (HPBO) copolymer, were toughened using dispersed rubbery phases generated by the sol-gel process. These rubbery phases were introduced using combinations of sol-gel precursors with varying numbers of alkyl groups. Scanning electron micrographs showed uniformly dispersed particles in these composite materials. In poly(arylene ether)s, a significant increase in toughness and ultimate elongation were achieved for samples prepared from relatively large amounts of sol-gel precursor with higher numbers of alkyl groups. In HPBO samples having low levels of the rubbery phase, both toughness and ultimate elongation were increased with increasing the amount of rubbery phase. Improvements in these properties of the HPBO polymer are rather large compared to the poly(arylene ether) polymers. The results also demonstrated improved thermal properties and decreased water absorption.

(Keywords: Toughening; sol-gel process; high-temperature polymers; poly(arylene ether); poly(benzoxazole))

\* To whom correspondence should be addressed. E-mail: markje@email.uc.edu

## INTRODUCTION

The use of polymeric materials in the manufacture of aerospace structures has increased markedly in recent years. This is due to their many desirable characteristics, in comparison to traditional aerospace materials such as the metals aluminum and titanium. Their most desirable attribute is the ability to combine high strength and stiffness with low density<sup>1</sup>.

Of particular interest are "high-performance polymers" which possess a combination of excellent mechanical properties such as high strength, high stiffness and high impact resistance, and maintain these properties at extremes of temperature. Other properties such as low dielectric constants, chemical and solvent resistance, and low flammability of these polymers are also desired<sup>2</sup>. There is an increasingly high demand for such polymers in the aerospace industry for the projected manufacture of high-speed commercial transport aircraft<sup>3</sup>. For example, Boeing's market projections indicate a significant demand for civil aircraft carrying 250-300 passengers over distances up to 8000 km and flying at supersonic speeds between Mach 2.0 and 2.4. At such high speeds, the aircraft would be exposed to very high temperatures<sup>2</sup>. This will require new polymeric composites which will incorporate more plastics to reduce total platform and payload weight and still allow performance at very high speeds.

Polycarbonate and poly(methylmethacrylate) thermoplastic polymers already provide excellent transparency and impact properties for current military aircraft canopies, windows and windscreens<sup>4</sup>. However, the use of these materials at very high temperatures is impossible because of their low softening temperatures and low thermal stabilities. Thus, transparent high-temperature polymers are considered as possible candidates for such applications as well<sup>2</sup>. These polymers contain aromatic or heteroaromatic units in their backbone, and

these units provide exceptional thermal and chemical stabilities. However, these units are rigid and can cause the polymers to exhibit high degrees of brittleness. Therefore, high-temperature polymers need to be toughened for applications in advanced structural composites and other neat-resin applications, including canopies.

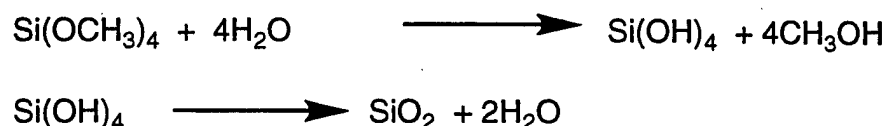
The technique of toughening a brittle polymer by introducing a rubbery second phase has been known for more than two decades. Simple physical blending of the polymer with a second rubbery phase, however, leads to a material with poor mechanical properties, and the dispersed phase can cause loss of transparency due to a coarse dispersed phase morphology and poor interfacial adhesion<sup>5-7</sup>. Compatibilization is needed to convert such immiscible blends into commercially useful products. An appropriate compatibilizer could be a block or graft copolymer with one portion identical to or miscible with the polymer phase. A successful compatibilizer will permit finer dispersion of the second phase during mixing, stabilize the structure and improve interfacial adhesion<sup>8</sup>.

Various types of elastomers have been employed as the rubbery second phase providing toughening effects in both thermoplastics and thermosets<sup>9-11</sup>. Diene polymers such as natural rubber and its copolymers<sup>12</sup> involving monomers such as butadiene are frequently used as the rubbery phase to obtain toughening. Their unsaturated structures can be an advantage with regard to reactions providing bonding between the phases, but also cause losses in stability, especially at high temperatures. Therefore, there is considerable interest in using totally-saturated elastomers.

In the present study, the high-temperature polymers investigated were two poly(arylene ether)s and a hydroxypoly(benzoxazole) copolymer, and they were toughened using siloxane-type rubbery phases. Of particular interest here is the

fact that poly(arylene ether) polymers have been evaluated as potential high-transparency materials<sup>4</sup>. On the other hand, the hydroxy functional group in the poly(benzoxazole) polymer gives the added advantage that it can be used to facilitate the bonding between the two phases through the use of a bonding agent<sup>13,14</sup>. The siloxane-type rubbery phase was generated in-situ using the sol-gel process.

This process<sup>15</sup> has been widely used to prepare organic-inorganic hybrid materials with unique combinations of properties from both organic and inorganic components<sup>16</sup>. In such cases, the organic polymer was reinforced by the secondary ceramic phase (e.g. silica). The preparation technique is based on the in-situ generation of ceramic phases within the organic polymer by the sol-gel process using organometallic precursors such as tetramethoxysilane (TMOS)<sup>16</sup>. The two steps of the sol-gel process, hydrolysis and condensation, for TMOS are



These reactions are catalyzed by acids, bases or salts<sup>16</sup>. Use of the sol-gel process for the preparation of organic-inorganic composites with high-temperature polymers as the organic phase<sup>17,18</sup> presents many difficulties, however. For instance, because of their intractability, most high-temperature polymers are virtually impossible to process. In addition, due to their unreactivity (which is desired in most of their applications), bonding between the organic polymer phase and the inorganic ceramic phase is generally not possible. This can cause phase separation, with the resulting materials having properties less

than expected. In order to minimize this undesirable phase separation, functionalized polymers can be used, with the two phases being bonded through the use of a bonding agent<sup>13,14,19,20</sup>.

The primary interest in the present research was to toughen brittle high-temperature polymers by a secondary rubbery phase. This was achieved by in-situ generating organically-modified silica particles by the sol-gel technique within the polymer matrix. More specifically, the brittleness of the silica particles, which are generally used to reinforce polymers, was reduced by incorporating alkyl groups into the generated particles. For this purpose, mixtures of sol-gel precursors alkyltrialkoxysilanes  $R'Si(OR)_3$ , dialkyldialkoxysilanes  $R'R''Si(OR)_2$  and tetraalkoxysilanes  $Si(OR)_4$  were used instead of  $Si(OR)_4$  alone. Hydrolysis and condensation of  $R'Si(OR)_3$  and  $R'R''Si(OR)_2$  yield less rigid products since the particles contain non-hydrolyzable  $R'$  and  $R''$  groups, which give the generated phases the deformability associated with toughness<sup>21</sup>.

The resulting materials were characterized with regard to their structures, mechanical properties (modulus, ultimate strength, maximum extensibility, and toughness), thermal properties, optical properties, and tendencies to absorb water.

## EXPERIMENTAL DETAILS

### *Materials*

The polymers used as the continuous phase were two poly(arylene ether)s (designated 6F-ETPP-E and FEK-E), and a hydroxypoly(benzoxazole) copolymer (HPBO). They were prepared at the Wright-Patterson Air Force Base<sup>4</sup>, and their structures are shown in Figure 1. The organosilanes tetramethoxysilane (TMOS) (99+%), methyltrimethoxysilane (MTMOS) (99+%), and dimethyldimethoxysilane (DMDMOS) (99+%) were purchased from United

Chemical Technologies, Inc. Anhydrous tetrahydrofuran (THF) was purchased from the Aldrich Chemical Company, and diethylamine from Fisher, Inc. The bonding agent used for the HPBO polymer, isocyanatopropyltriethoxysilane (95%), was also purchased from United Chemical Technologies, Inc.

#### *Sample preparation*

##### *Poly(arylene ether)s*

The polymers 6F-ETPP-E and FEK-E were dried in a vacuum oven at 120 °C to remove any water, and the desired amount of each polymer was dissolved in anhydrous THF. After clear solutions were obtained, the chosen amounts of TMOS and DDMOS were added. The mixtures were stirred at room temperature to again give clear solutions. Stoichiometric amounts of a 5 wt% diethylamine aqueous solution were then added and the mixtures were further stirred at room temperature to ensure homogeneous mixing. The resulting viscous solutions were transferred to Petri dishes for further hydrolysis and condensation. Evaporation of volatiles gave films, which were slowly dried in air. They were further dried under vacuum at 60 °C for 2 days. A series of samples were thus prepared from each polymer by varying the amounts of sol-gel precursors. Preparative information is given in Tables 1 and 2.

##### *Hydroxypoly(benzoxazole) copolymer*

The procedure for preparing composites from the HPBO polymer is similar to that followed for the poly(arylene ether) composites. However, in the case of HPBO, after dissolving the polymer in anhydrous THF the bonding agent isocyanatopropyltriethoxysilane was added (in stoichiometric amounts relative to the number of OH groups in the copolymer). A series of samples with varying amounts of the dispersed secondary phase was thus prepared. These dispersed

phases were generated within the polymer matrix by using different combinations of the sol-gel precursors, TMOS, MTMOS and DMDMOS. A summary of the information on the HPBO composite samples is given in Table 3.

#### *Scanning electron microscopy*

Scanning Electron Microscopy (SEM) was used to characterize both the film surfaces and their cross sections. Specimens were coated with gold, mounted on aluminum mounts, and then examined using a Model 90 Cambridge instrument. Energy Dispersive X-ray Analysis (EDAX) measurements accompanied by silicon atom distribution maps on the same samples were obtained using an EDS system (Princeton Gamma Tech).

#### *Mechanical properties*

Moduli, ultimate strengths and maximum extensibilities were measured at room temperature using an Instron mechanical tester. Samples with dimensions approximately  $50 \times 5 \times 0.2 \text{ mm}^3$  were tested at a cross-head speed of 0.1 in/min.

#### *Thermogravimetric analysis*

Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer model TAS-7 system at a heating rate of 20 °C, under a nitrogen atmosphere.

#### *Water absorption*

The extents of water absorption by the films under saturated conditions were measured by the method described in ASTM-D570-81. In brief, the films were dried at 120 °C in vacuum over night, weighed and immersed in distilled water, with periodic reweighings until the weight became constant.

## RESULTS AND DISCUSSION

### *Morphology*

In most cases, the samples had some transparency, indicating good dispersion of the second phase. Figure 2 shows this, as a picture of vertically-mounted strips of 6F-ETPP-E polymer with 10 wt% rubbery phase but with varying proportions of the sol-gel precursors used to generate the dispersed phase. Increasing the proportion of the flexibilizing DMDMOS is seen to decrease the transparency.

Figures 3-5 show the scanning electron micrographs of unfractured and fractured surfaces of some selected samples. SEM pictures of the unfractured surfaces of the pure 6F-ETPP-E polymer and the sample having 10 wt% rubbery phase from 1:1 mole ratio of TMOS:DMDMOS are shown in Figure 3 (a) and (b), respectively. Figure 3 (b) shows well-dispersed uniform rubbery particles in the hybrid material. The particle distribution in the sample having 10 wt% rubbery phase from 1:3 mole ratio of TMOS:DMDMOS (Figure 4) indicates that the particle size in this sample is larger than that in the sample with the same amount of rubbery phase generated using a 1:1 mole ratio of TMOS:DMDMOS. This could be due to the increased number of organic groups in the dispersed phase obtained from the 1:3 mole ratio of TMOS:DMDMOS compared to that from the 1:1 mole ratio. Figure 5 (a) and (b) shows the scanning electron micrographs of the fractured surfaces of the pure 6F-ETPP-E polymer and the sample having 10 wt% rubbery phase from the 1:1 mole ratio, respectively. As expected, the fractured surface of the sample having rubbery particles is somewhat coarse, compared to that of the pure polymer.

The EDAX spectra for the 6F-ETPP-E pure polymer and that for the 6F-ETPP-E sample with 10 wt% rubbery phase from a 1:1 mole ratio of TMOS:DMDMOS are given in Figures 6 and 7. The silicon distribution maps for



the fractured and unfractured surfaces of the 6F-ETPP-E sample with 10 wt% rubbery phase from a 1:1 mole ratio of TMOS:DMDMOS are given in Figures 8 (a) and (b), respectively. Figures 7 and 8 clearly show uniformly distributed silica confirming that the rubbery phase is dispersed homogeneously in the material.

### *Mechanical properties*

Some of the mechanical properties of the 6F-ETPP-E pure polymer and the samples with 10 wt% rubbery phase prepared using varying TMOS:DMDMOS mole ratios are described in Figure 9 and Table 4. Compared to that of the pure polymer, the moduli of the samples from the 3:1, 2:1 and 1:1 mole ratios of TMOS:DMDMOS have been slightly increased, but those having 1:2 and 1:3 mole ratios have been decreased. The ultimate strengths of the samples with a rubbery phase have been slightly decreased compared to the pure polymer except for the sample corresponding to 1:2 mole ratio. Some substantial increases in ultimate elongation have been obtained, however. As a result, the toughness as measured by the area under the stress-strain curve was increased for all the samples except for the samples from the 3:1 and 2:1 mole ratios. This decrease in the toughness and the ultimate elongation for the samples corresponding to these higher amounts of TMOS could have been anticipated, since the relative amounts of glassy silica in the second phase were higher in these samples. The significant increases in toughness and ultimate elongation, and the decrease in moduli for the samples prepared from 1:2 and 1:3 mole ratios are all presumably due to the considerable increase in the rubbery properties of the silica particles from the alkyl groups they contain. Most impressively, more than two-fold increases in toughness were achieved for samples corresponding to 1:1 and 1:3 mole ratios of TMOS:DMDMOS.

The mechanical properties for the FEK-E pure polymer and the samples prepared from it having 10 wt% of the dispersed phase from various TMOS:DMDMOS mole ratios are given in Figure 10 and Table 5. The sample corresponding to 1:2 mole ratio of TMOS:DMDMOS showed a slight increase in modulus and the other composite samples showed no noticeable change at all. The toughness and ultimate elongation of the sample corresponding to 2:1 mole ratio of TMOS:DMDMOS have been decreased with compared to those of the pure polymer. This could be due to the relatively higher amount of silica in the secondary phase in this sample. There is a significant increase in the toughness and ultimate elongation of the samples corresponding to 1:2 and 1:3 mole ratios, however, and this increase is particularly striking for the latter sample. This demonstrates that the larger the number of alkyl groups in the modified dispersed phase, the more pronounced its rubbery properties, and therefore the larger the toughening effect.

Figure 11 and Table 6 describe the mechanical properties of the HPBO pure polymer and the samples from it containing varying amounts of the rubbery phase from a 1:1 mole ratio of TMOS:MTMOS. There is a slight decrease in moduli of these samples compared to that of the pure polymer. Incorporation of the rubbery phase into the HPBO polymer, however, has significantly increased the ultimate elongation and toughness except for the sample having the 20 wt% rubbery phase. The decrease in ultimate elongation and toughness of the sample with the 20 wt% rubbery phase may be due to possible phase separation when large amounts of the second phase are introduced. The ultimate strengths of these materials do not show any obvious trend with increase in the amount of rubbery phase. By incorporating a small amount of the rubbery phase (e. g., 5 wt%), the ultimate elongation and the toughness were increased to a large extent; however, further incorporation of the rubbery phase did not increase the

ultimate elongation proportionally. Improvements in ultimate elongation and toughness of the HPBO polymer are rather large compared to that of the 6F-ETPP-E polymer. This may be due to the interfacial bonding between the phases being improved by the use of the bonding agent in the case of the HPBO polymer.

Figure 12 shows stress-strain curves for some HPBO samples with varying amounts of the second phase, which was generated using all three sol-gel precursors TMOS, MTMOS and DMDMOS in 1:1:1 mole ratio. In this case, the moduli of all three samples having different amounts of rubbery phase were again slightly decreased relative to that of the pure HPBO polymer. However, in this case the improvements in ultimate elongation and toughness are smaller than in the previous case (with the rubbery phase generated using a 1:1 mole ratio of TMOS:MTMOS).

#### *Thermal stability*

The TGA curves for the FEK-E polymer and its composite having 10 wt% rubbery phase from the 1:3 mole ratio of TMOS:DMDMOS are given in Figure 13. The transition temperature at which the drastic weight loss occurs has been raised by about 50 °C for this FEK-E composite compared to that for the pure FEK-E polymer suggesting improved thermal stability through the incorporation of the second phase. In addition, the weight residue at 800 °C of this sample is higher compared to that of the pure sample.

#### *Water absorption*

Figure 14 shows the extent of water absorption for 6F-ETPP-E samples having a 10 wt% rubbery phase. In all the cases, the extent of water absorption is decreased in comparison to that for the pure sample. According to the results,

the larger the amount of DMDMOS used relative to TMOS, the lower the water absorptivity. This could be explained by the increased amount of hydrophobic alkyl groups in the samples from the larger amounts of DMDMOS relative to TMOS. The decreased absorption could be very important with regard to dimensional stability and improved dielectric properties.

## CONCLUSIONS

Morphology studies indicated uniformly dispersed rubbery particles in the composites investigated. For the poly(arylene ether)s, a significant increase in toughness and ultimate elongation were achieved for the samples prepared from relatively larger amounts of sol-gel precursors having larger numbers of alkyl groups. In the HPBO samples having low levels of the rubbery phase, both toughness and ultimate elongation were increased with increasing the amount of rubbery phase without causing any significant change in the modulus. Improvements in these properties of the HPBO polymer are rather large compared to those of 6F-ETPP-E polymer. This may be due to the interfacial bonding between the phases being improved by the use of the bonding agent in the case of the HPBO polymer. The results also indicated improved thermal properties and decreased water absorption of the composites.

## ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the financial support provided by the Air Force Office of Scientific Research (Directorate of Chemistry and Materials Science) through Grants F49620-96-10052 and F49620-96-10235.

## REFERENCES

1. Shaw, S. J., in *Rubber Toughened Engineering Plastics*, ed. A. A. Collyer, Chapman and Hall, Washington, DC, 1994.
2. Hodd, K., *TRIP*, 1993, **1(5)**, 129.
3. Hergenrother, P. M., *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, 1992, **33(1)**, 354.
4. Unroe, M. R., Gupta, R. K., Sharma, R. B. and Thiesing, N. C., *Polym. Preprints, Am. Chem. Soc., Div. Polym. Chem.*, 1997, **38 (2)**, 293.
5. Cimmino, S., D'Orazio, L., Greco, R., Maglio, G., Malinconico, M., Mancarella, C., Martuscelli, E., Palumbo, R. and Ragosta, G., *Polym. Eng. Sci.*, 1984, **24**, 48.
6. Ide, F. and Hasegawa, A. *J. Appl. Polym. Sci.*, 1974, **18**, 963.
7. La Mantia, F. P. and Valenza, A., *Eur. Polym. J.*, 1989, **24**, 553.
8. Li, D., Wang, H.-C. and Yee, A. F., *Polymeric Materials Encyclopedia*, ed. J. C. Salamone, CRC Press, Inc, Boca Raton, FL, 1996, p. 5409.
9. *Rubber-Toughened Plastics*, ed. C. K. Riew, American Chemical Society, Washington, DC, 1989, vol. 222.
10. *Toughened Plastics I*, eds. C. K. Riew and A. J. Kinloch, American Chemical Society, Washington, DC, 1993, vol. 233.
11. *Rubber-Toughened Engineering Plastics*, ed. A. A. Collyer, Chapman & Hall, Washington, DC, 1994.
12. Ishikawa, M., *Polymer*, 1995, **36**, 2203.
13. Premachandra, J., Kumudinie, C., Zhao, W., Mark, J. E., Dang, T. D., Chen, J. P. and Arnold, F. E., *J. Sol-Gel Sci. Technol.*, 1996, **7**, 163.
14. Mark, J. E., Premachandra, J., Kumudinie, C., Zhao, W., Dang, T. D., Chen, J. P. and Arnold, F. E. in *Better Ceramics Through Chemistry VII: Organic/Inorganic Hybrid Materials*, eds. B. K. Coltrain, C. Sanchez, D. W.

- Schaefer, and G. L. Wilkes, Materials Research Society, Pittsburgh, 1996, vol. 435, p. 93.
15. Brinker, C. J. and Scherer, G. W., *Sol-Gel Science*, Academic Press, New York, 1990.
  16. *Hybrid Organic-Inorganic Composites*, eds. J. E. Mark, C. Y.-C. Lee, and P. A. Bianconi, American Chemical Society, Washington, DC, 1995, vol. 585.
  17. Mark, J. E., Wang, S. and Ahmad, Z., *Macromol. Symp.*, 1995, **98**, 731.
  18. Ahmad, Z., Wang, S. and Mark, J. E., in *Better Ceramics Through Chemistry VI*, eds. A. Cheetham, C. J. Brinker, M. L. Mecartney, and C. Sanchez, Materials Research Society, Pittsburgh, PA, 1994, vol. 346, p. 127.
  19. Premachandra, J., Kumudinie, C., Mark, J. E., Dang, T. D. and Arnold, F. E., *J. Macromol. Sci., Pure Appl. Chem.*, 1999, **A36(1)**, 73.
  20. Premachandra, J., van Ooij, W. J., and Mark, J. E., *J. Adhesion Sci. Technol.*, 1998, **12(12)**, 1361.
  21. Ning, Y.-P. and Mark, J. E., *Polym. Bulletin*, 1984, **12**, 407.

**Table 1** Sample information for the 6F-ETPP-E composites

Designation	Dispersed phase (wt%)	<u>Sol-gel precursors</u> TMOS:DMDMOS mole ratio
6F-ETPP-E-0	0	-
6F-ETPP-E-3:1	10	3:1
6F-ETPP-E-2:1	10	2:1
6F-ETPP-E-1:1	10	1:1
6F-ETPP-E-1:2	10	1:2
6F-ETPP-E-1:3	10	1:3

**Table 2** Sample information for the FEK-E composites

Designation	Dispersed phase (wt%)	<u>Sol-gel precursors</u> TMOS:DMDMOS mole ratio
FEK-E-0	0	-
FEK-E-3:1	10	3:1
FEK-E-2:1	10	2:1
FEK-E-1:1	10	1:1
FEK-E-1:2	10	1:2
FEK-E-1:3	10	1:3



**Table 3** Sample information for the HPBO composites

Designation	Dispersed phase (wt%)	<u>Sol-gel precursors</u>	
		TMOS:MTMOS mole ratio	TMOS:MTMOS:DMDMOS mole ratio
HPBO-0	0	-	-
HPBO-5-1:1	5	1:1	-
HPBO-15-1:1	15	1:1	-
HPBO-20-1:1	20	1:1	-
HPBO-5-1:1:1	5	-	1:1:1
HPBO-15-1:1:1	15	-	1:1:1
HPBO-20-1:1:1	20	-	1:1:1

**Table 4** Mechanical properties of the 6F-ETPP-E composites

<u>Rubbery phase</u>		Modulus (MPa)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
wt%	Sol-gel precursor <sup>a</sup>				
0	--	1820	35.3	4.3	1.17
10	TMOS:DMDMOS (3:1)	1900	24.4	1.2	0.18
10	TMOS:DMDMOS (2:1)	1940	33.4	2.7	0.59
10	TMOS:DMDMOS (1:1)	1940	34.0	9.4	2.69
10	TMOS:DMDMOS (1:2)	1580	36.3	6.7	2.05
10	TMOS:DMDMOS (1:3)	1370	32.8	10.4	2.81

<sup>a</sup>Molar ratios of the corresponding precursors are given in parenthesis

**Table 5** Mechanical properties of the FEK-E composites

<u>Rubbery phase</u>		Modulus (MPa)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
wt%	Sol-gel precursor <sup>a</sup>				
0	--	1630	62.2	4.9	1.62
10	TMOS:DMDMOS (2:1)	1670	53.1	4.2	1.41
10	TMOS:DMDMOS (1:2)	1890	47.9	15.5	6.39
10	TMOS:DMDMOS (1:3)	1670	62.4	24.7	11.1

**Table 6** Mechanical properties of the HPBO composites

wt%	<u>Rubbery phase</u>		Modulus (MPa)	Ultimate strength (MPa)	Ultimate elongation (%)	Toughness (MPa)
	Sol-gel	precursors <sup>b</sup>				
0	--		2140	69.1	8.9	4.95
5	TMOS:MTMOS	(1:1)	2040	66.7	20.9	12.8
15	TMOS:MTMOS	(1:1)	2120	68.7	24.3	15.8
20	TMOS:MTMOS	(1:1)	2050	67.0	7.6	3.84
5	TMOS:DMDMOS:		2100	67.0	13.3	8.08
	MTMOS	(1:1:1)				
15	TMOS:DMDMOS:		1980	63.9	14.3	9.28
	MTMOS	(1:1:1)				
20	TMOS:DMDMOS:		2070	63.9	11.9	6.37
	MTMOS	(1:1:1)				

## Legends for Figures

Figure 1. Structures of the high-temperature polymers: (a) 6F-ETPP-E, (b) FEK-E and (c) HPBO.

Figure 2. Strips of the 6F-ETPP-E pure polymer and the toughened samples with 10 wt% rubbery phases, demonstrating their transparencies: (a) pure polymer, and the samples prepared from TMOS/DMDMOS mole ratios of (b) 3:1, (c) 2:1, (d) 1:1, (e) 1:2 and (f) 1:3.

Figure 3. Scanning electron micrographs for the unfractured surfaces of (a) 6F-ETPP-E pure polymer and (b) the sample with 10 wt% rubbery phase prepared from a 1:1 mole ratio of TMOS:DMDMOS.

Figure 4. Scanning electron micrograph for the unfractured surface of the 6F-ETPP-E sample with 10 wt% rubbery phase prepared from a 1:3 mole ratio of TMOS:DMDMOS.

Figure 5. Scanning electron micrographs for the fractured surface of (a) 6F-ETPP-E pure polymer and (b) the sample with 10 wt% rubbery phase prepared from a 1:1 mole ratio of TMOS:DMDMOS.

Figure 6. The EDAX spectrum for the 6F-ETPP-E pure polymer.

Figure 7. The EDAX spectrum for the 6F-ETPP-E sample with 10 wt% rubbery phase prepared from a 1:1 mole ratio of TMOS:DMDMOS.

Figure 8. Silicon distribution maps for the 6F-ETPP-E sample with 10 wt% rubbery phase prepared from a 1:1 mole ratio of TMOS:DMDMOS: (a) unfractured surface and (b) fractured surface.

Figure 9. Stress-strain curves for 6F-ETPP-E pure polymer ( $\square$ ), and for samples containing 10 wt% rubbery phase from 3:1 ( $\nabla$ ), 2:1 (O), 1:1 ( $\blacklozenge$ ), 1:2 ( $\bullet$ ), and 1:3 ( $\Delta$ ) TMOS:DMDMOS mole ratios.

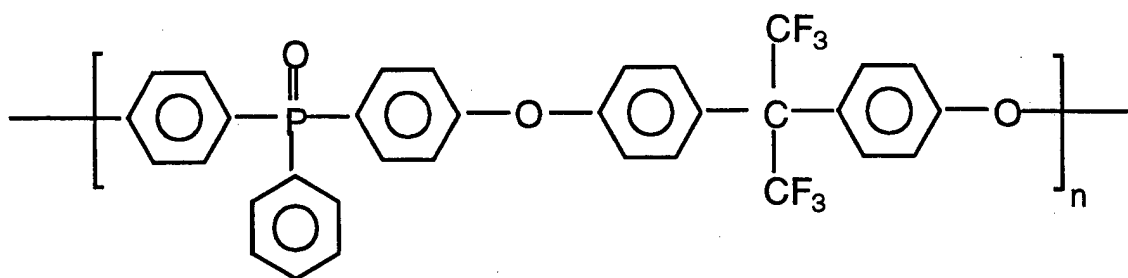
Figure 10. Stress-strain curves for FEK-E pure polymer ( $\square$ ), and for samples containing 10 wt% rubbery phase from 2:1 ( $\Delta$ ), 1:2 (O), and 1:3 ( $\bullet$ ) TMOS:DMDMOS mole ratios.

Figure 11. Stress-strain curves for HPBO pure polymer ( $\blacklozenge$ ), and for samples from a 1:1 mole ratio of TMOS:MTMOS with: 5 ( $\Delta$ ), 15 (O), and 20 ( $\bullet$ ) wt% rubbery phase.

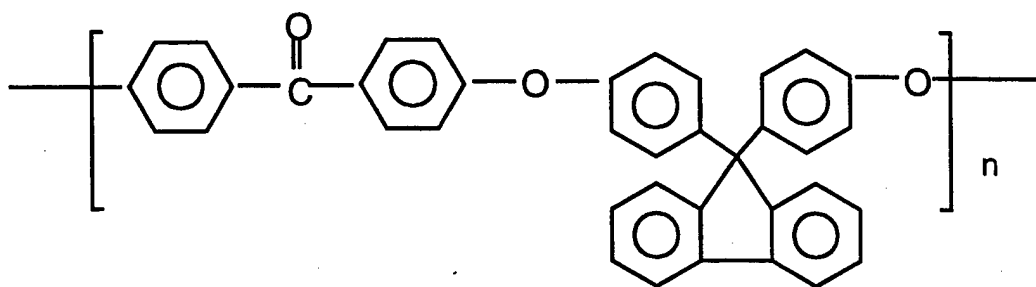
Figure 12. Stress-strain curves for HPBO pure polymer ( $\blacklozenge$ ), and for samples from a 1:1:1 TMOS:DMDMOS:MTMOS mole ratio: 5 ( $\Delta$ ), 15 (O), and 20 ( $\bullet$ ) wt% rubbery phase.

Figure 13. TGA curves for (a) FEK-E polymer and (b) its composite having 10 wt% rubbery phase from a 1:3 mole ratio of TMOS:DMDMOS.

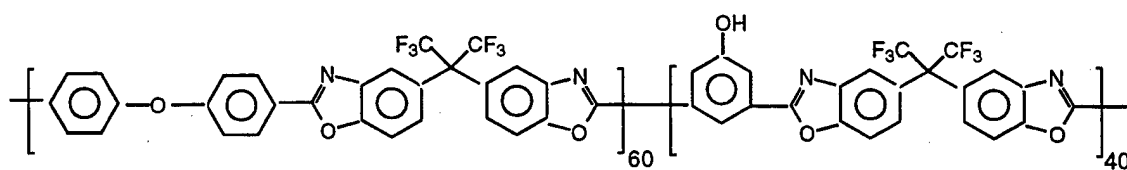
Figure 14. Extent of water absorption for the 6F-ETPP-E pure polymer (O), and for samples containing 10 wt % rubbery phase from 3:1 ( $\blacksquare$ ), 2:1 ( $\Delta$ ), 1:1 ( $\bullet$ ), 1:2 ( $\square$ ) and 1:3 ( $\blacktriangle$ ) TMOS:DMDMOS mole ratios.



(a)



(b)



(c)

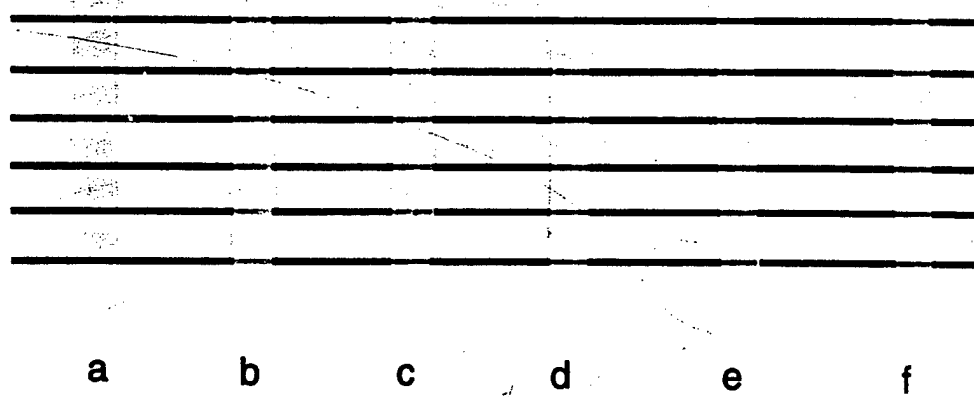
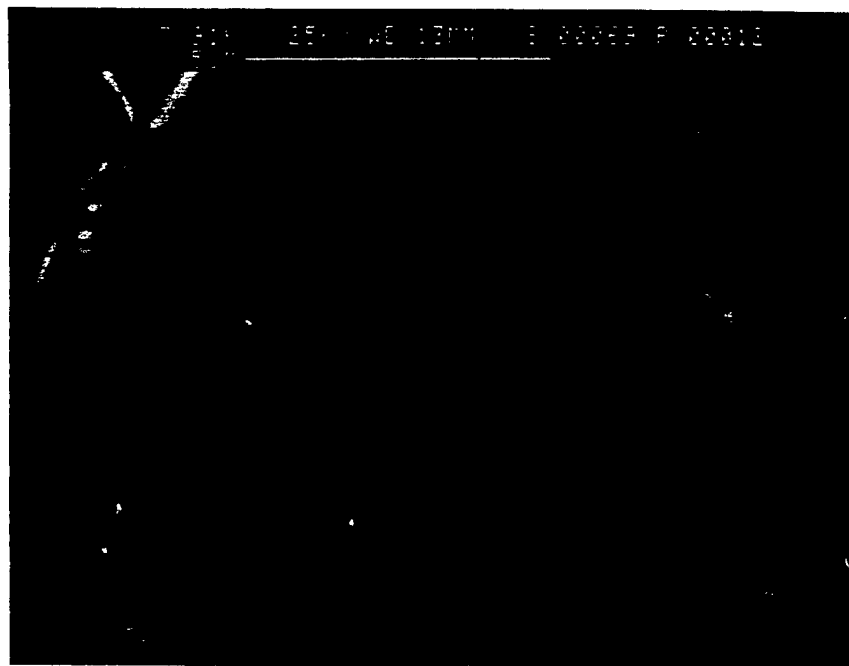
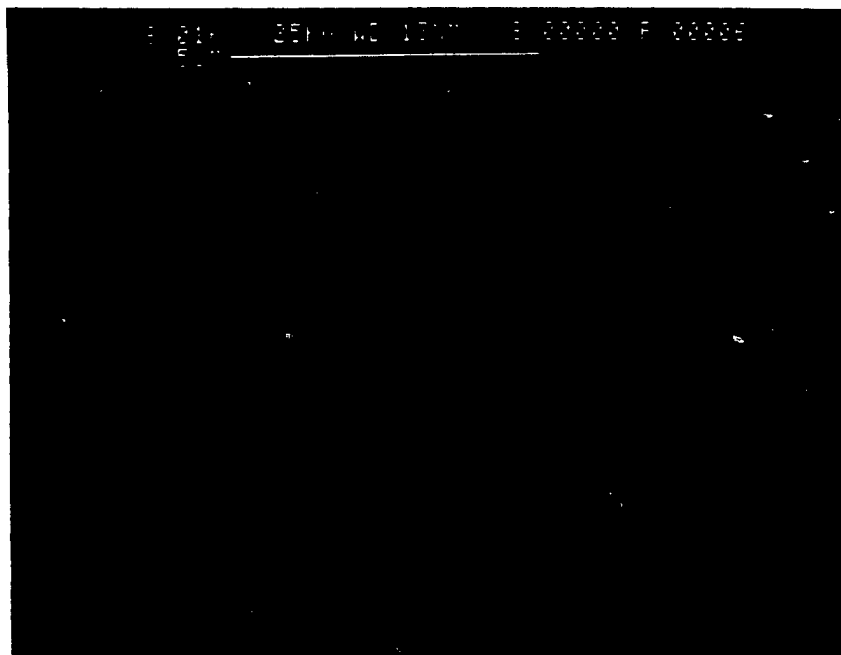


FIG. 2, KUMUDINIE .....





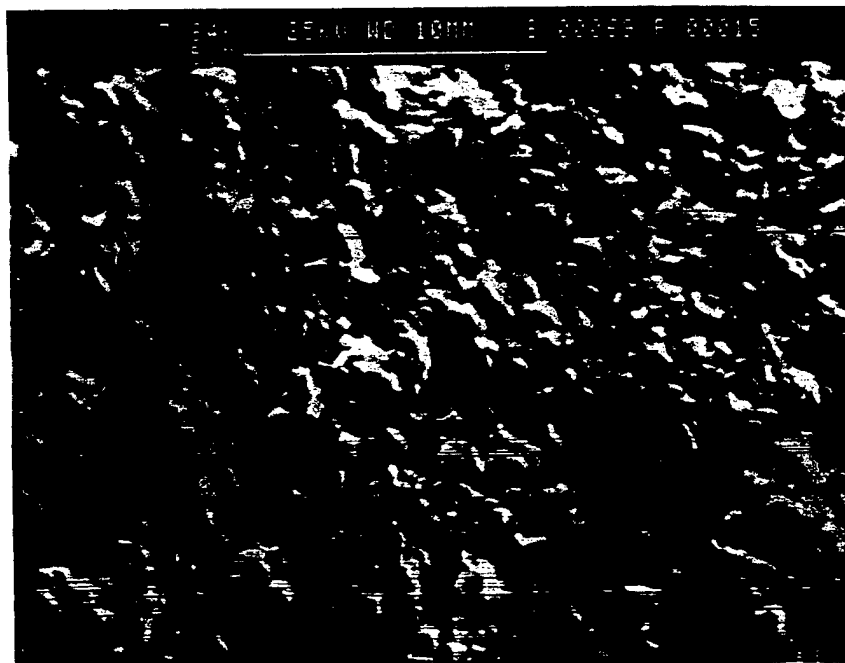
(a)



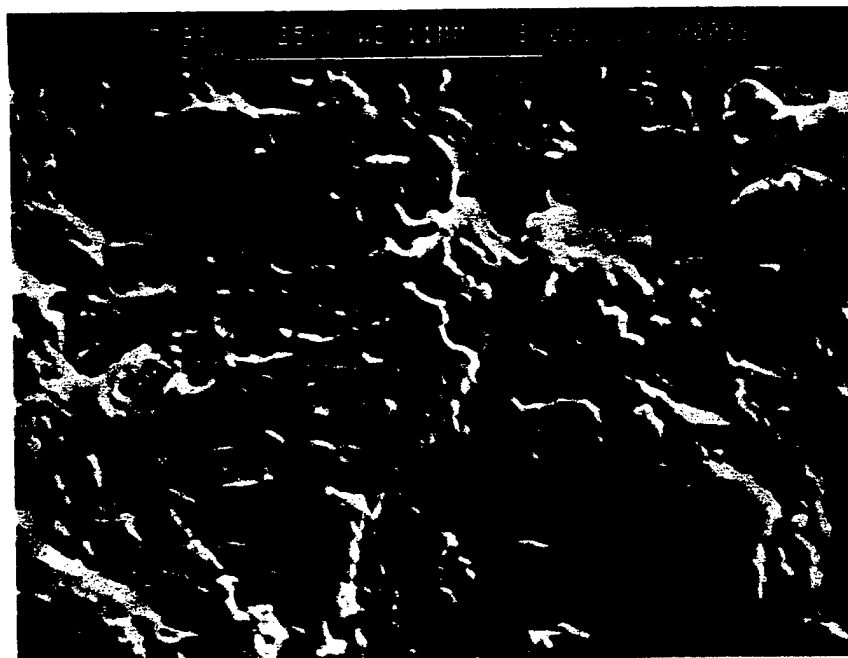
(b)



FIG. 4., KUMUDINIE....

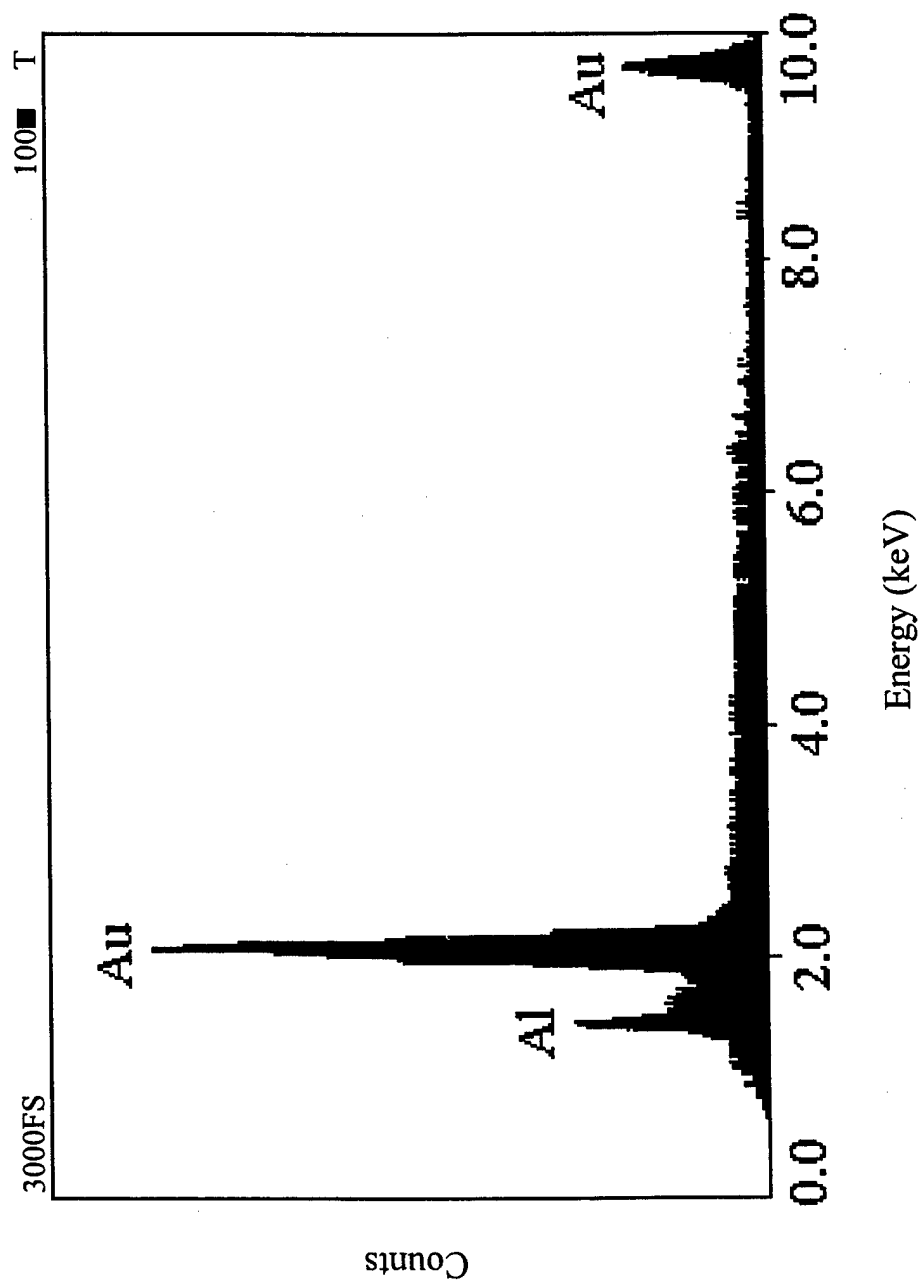


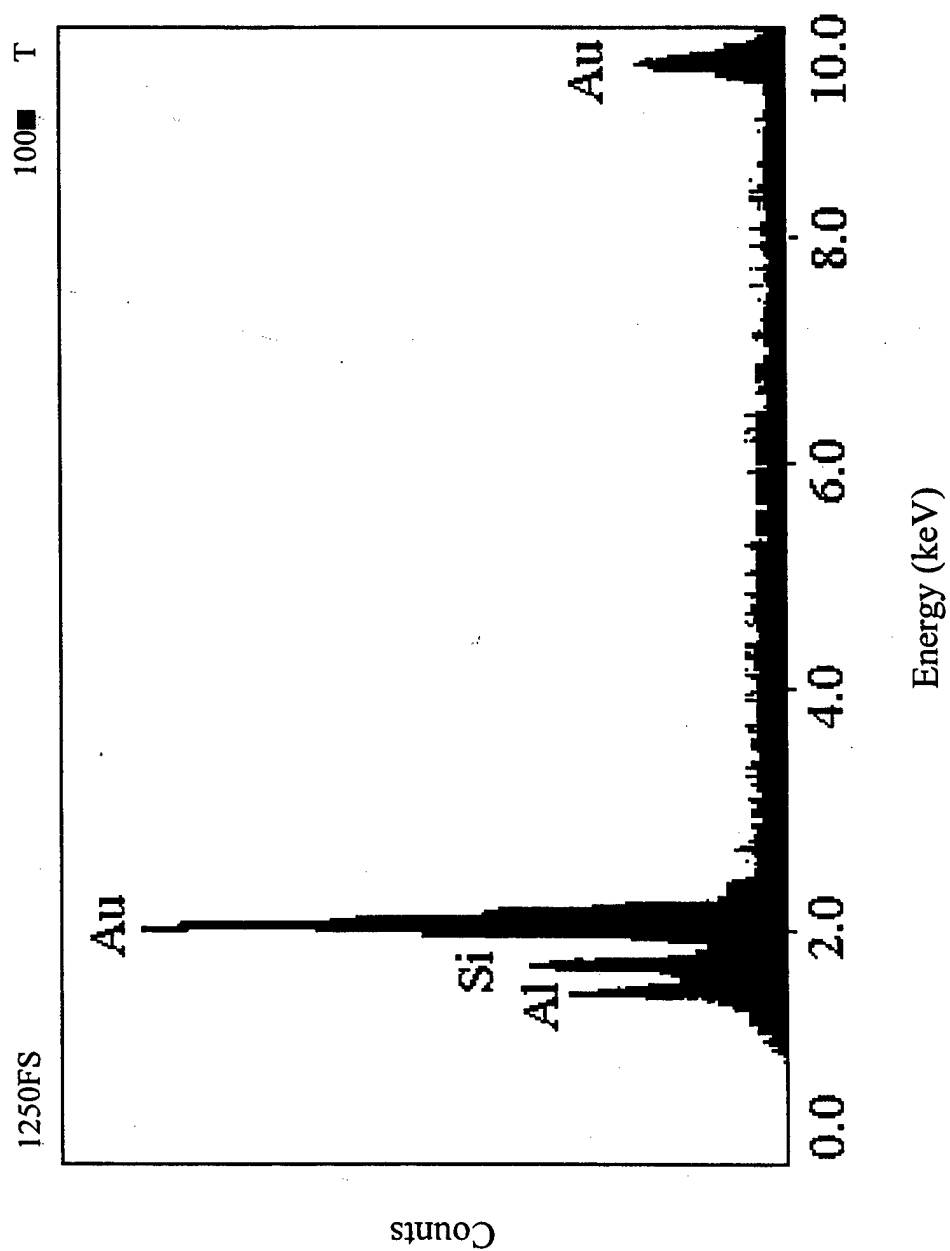
(a)

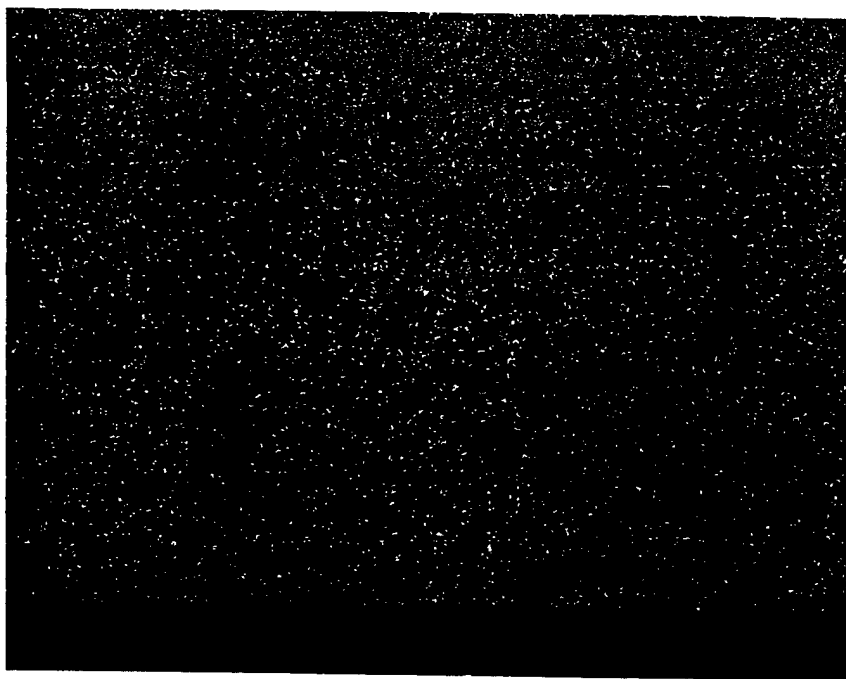


(b)

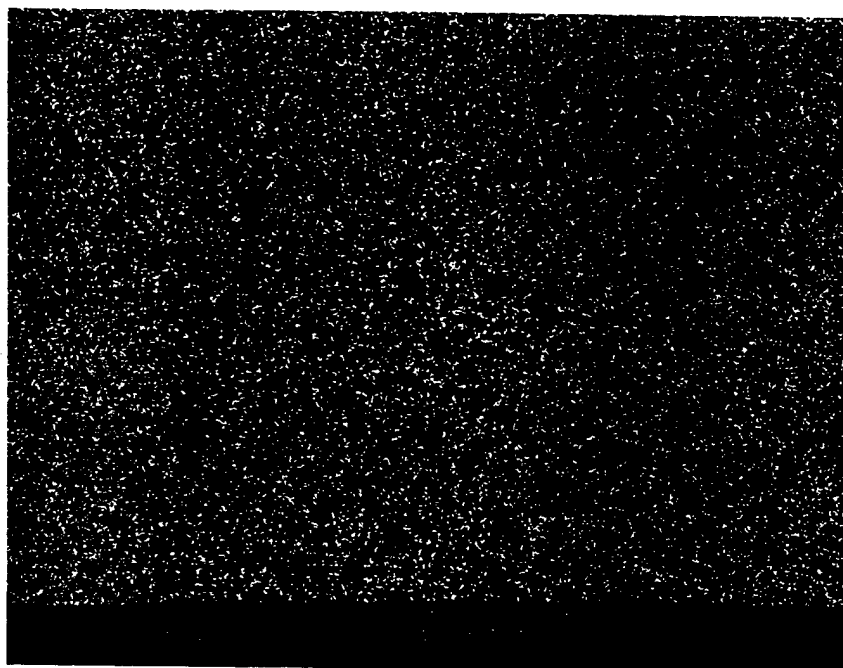
FIG. 5, KUMUDINIE....





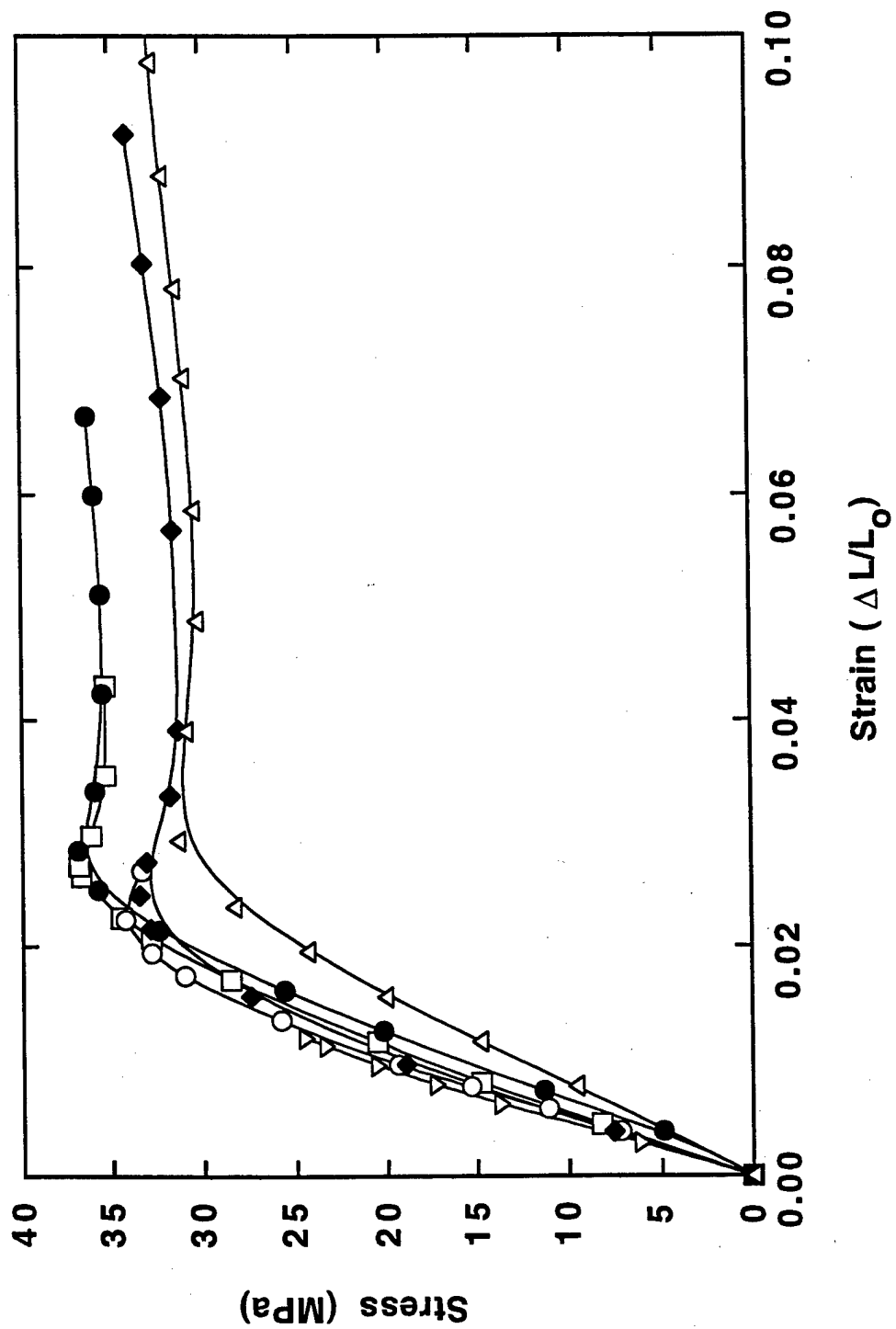


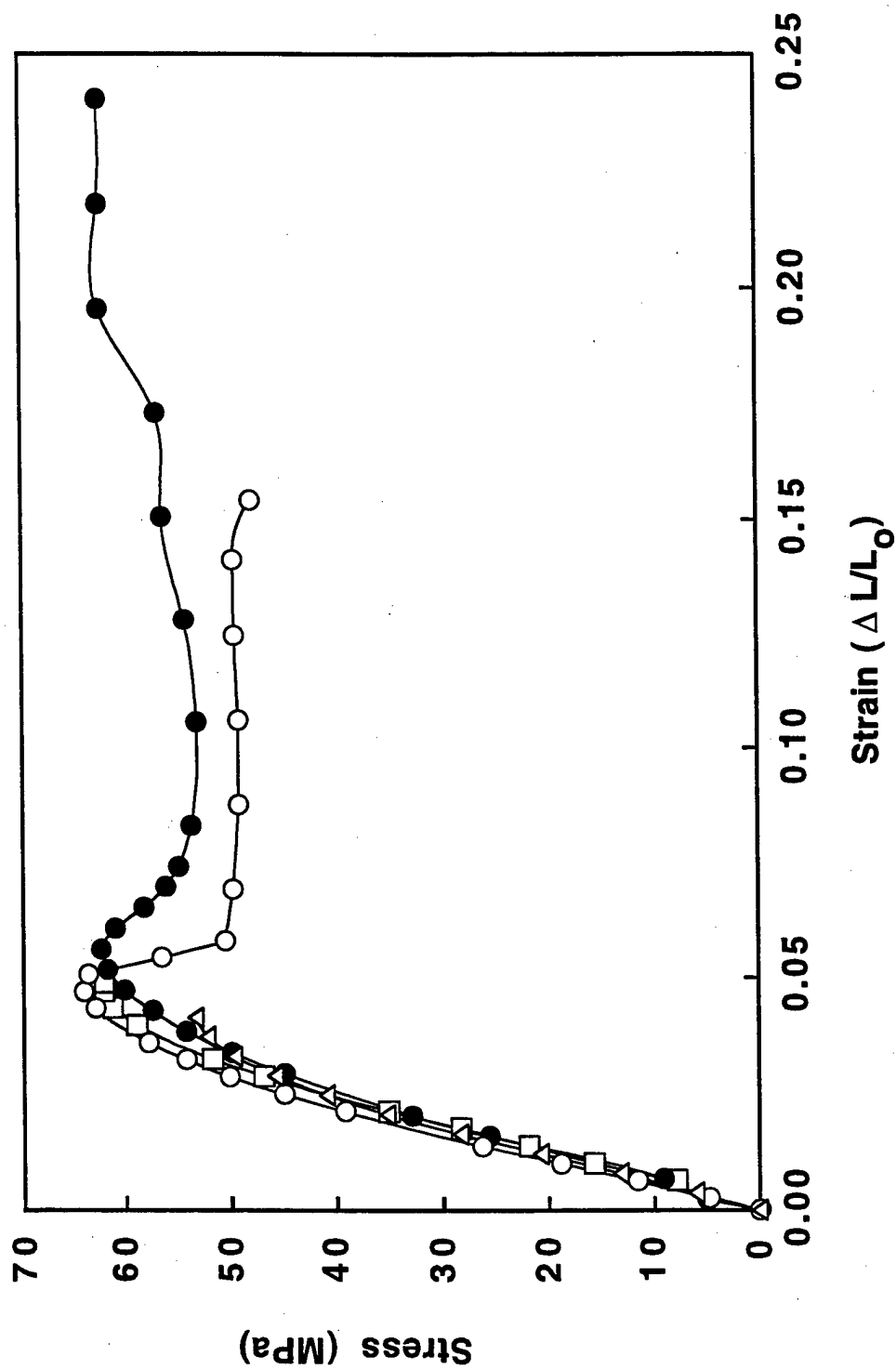
(a)



(b)

FIG. 8, KUMUDINIE . . .







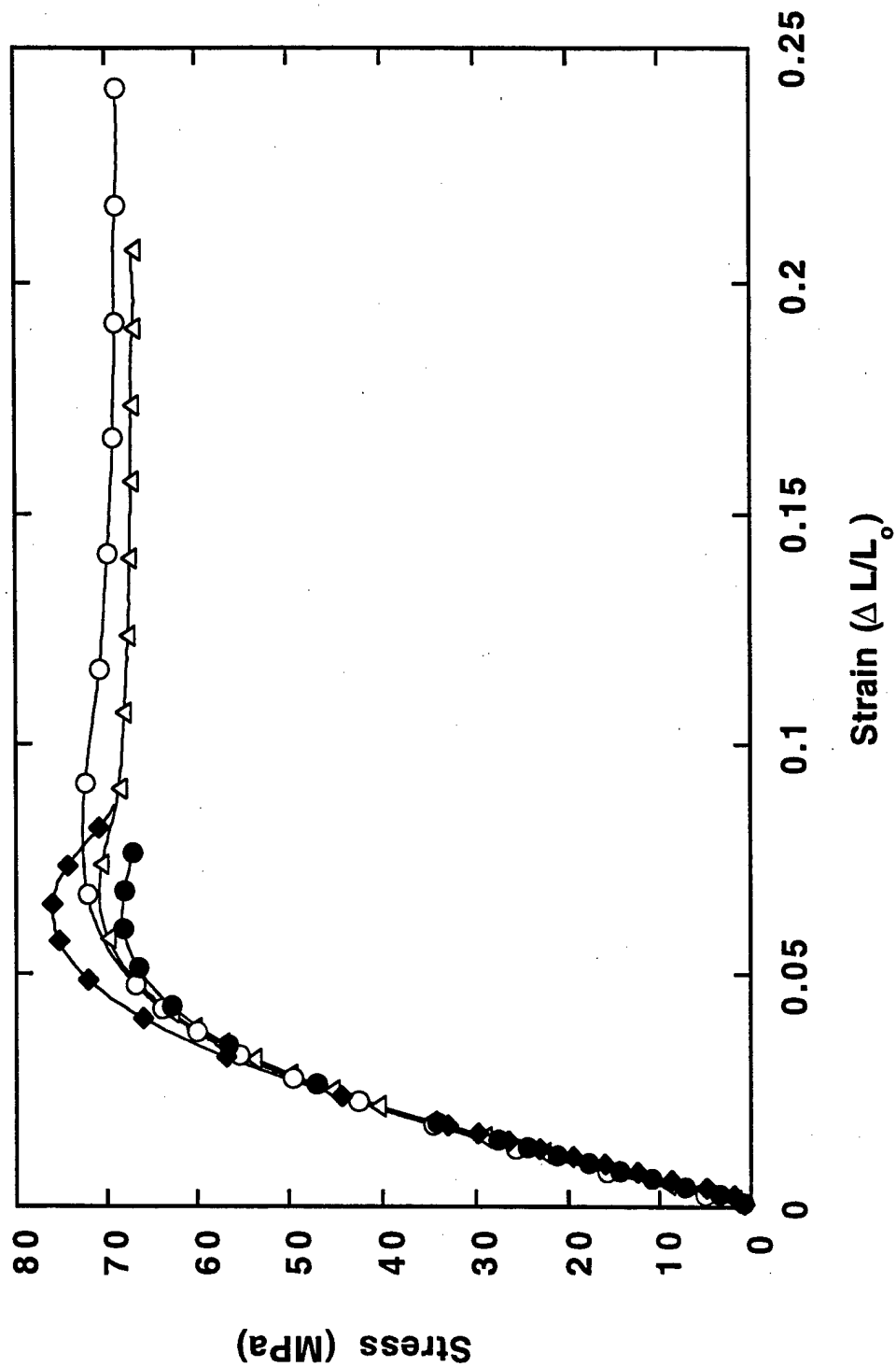


FIG. 11, KUMUDINIE ..

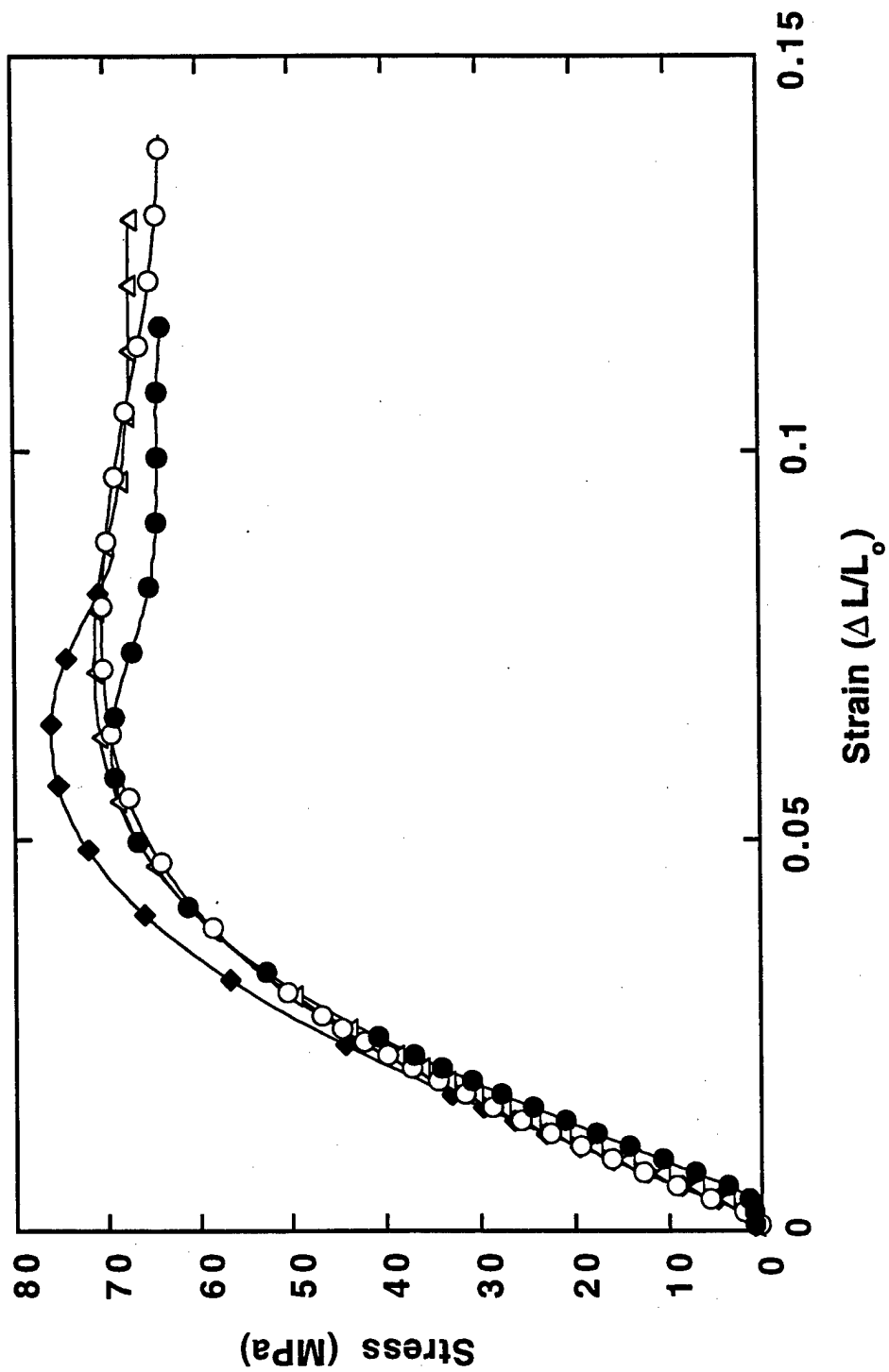
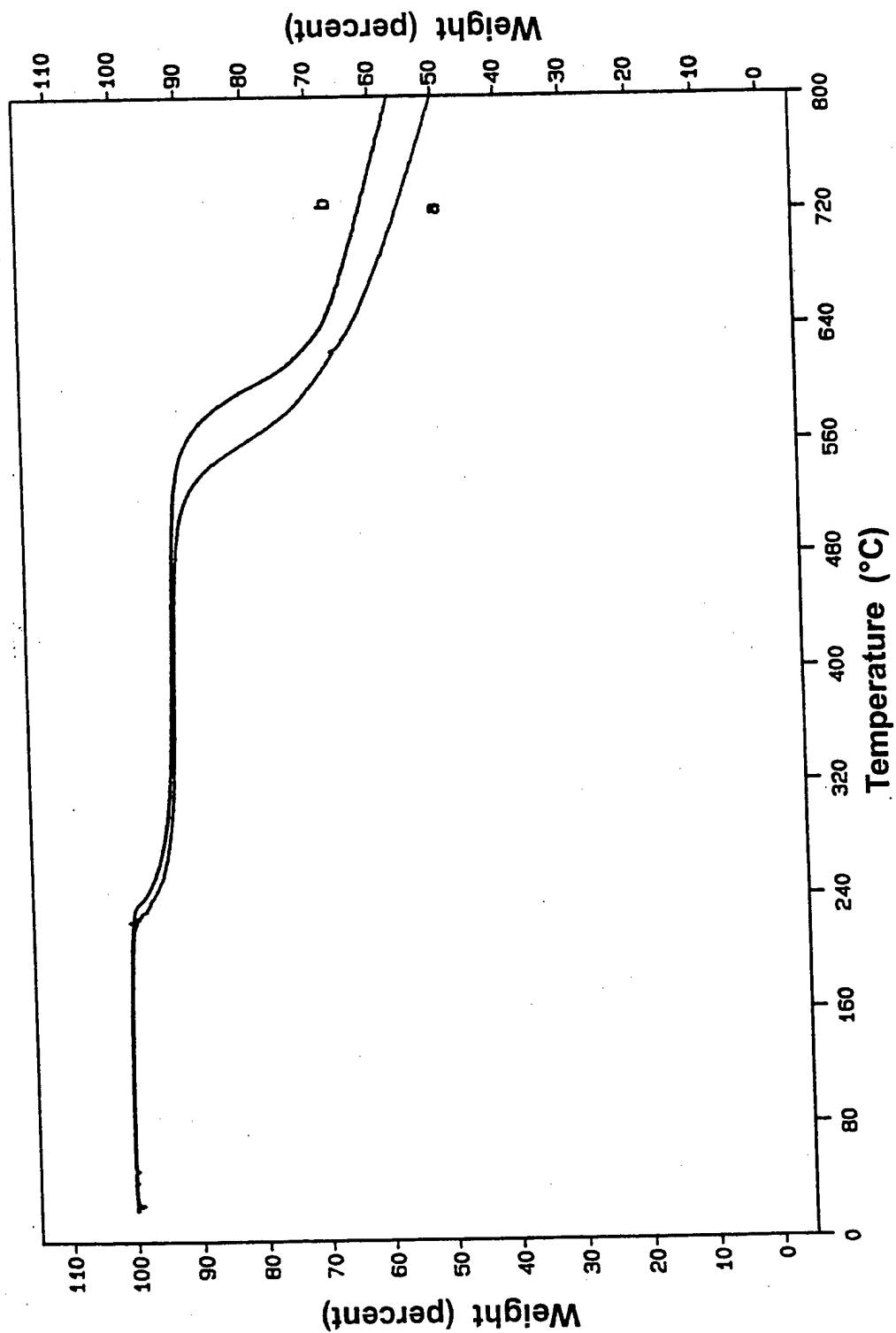


FIG. 12, KUMUDINIE ...



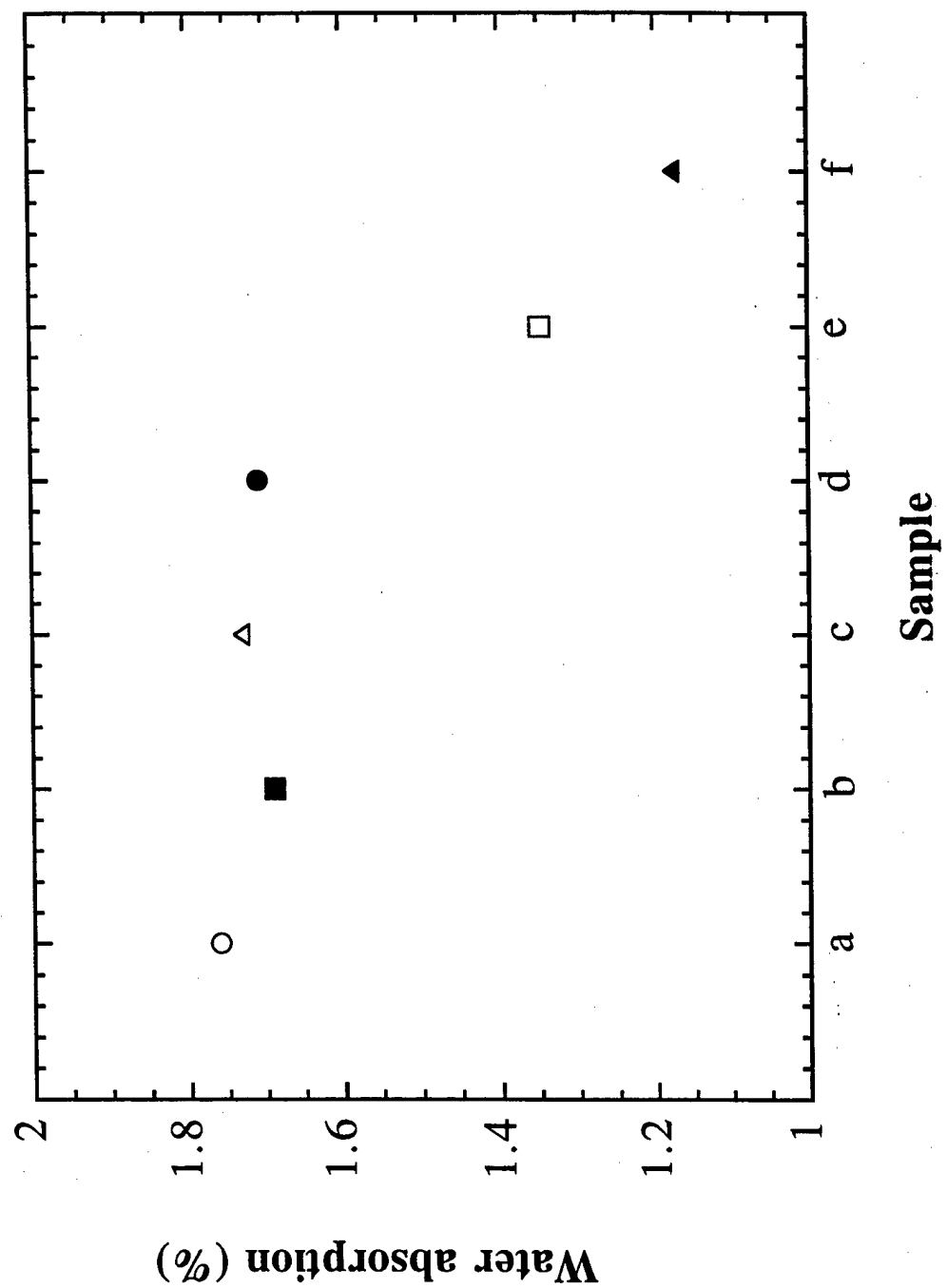


FIG. 14, KUMUDINIE...

## PREPARATION AND PROPERTIES OF SOME HYBRID AEROGELS FROM A SULFOPOLYBENZOBISTHIAZOLE-SILICA COMPOSITE

**J. K. Premachandra, C. Kumudinie, and J. E. Mark\***

Department of Chemistry and the Polymer Research Center  
University of Cincinnati  
Cincinnati, OH 45221-0172

**T. D. Dang and F. E. Arnold**

Polymer Branch  
AFRL/MLBP, B 654  
Wright-Patterson AFB, OH 45433-7750

**Key Words:** Aerogels, Organic-Inorganic Hybrid Materials, Polymer-Modified Ceramics, Sulfopolybenzobisthiazole, High-Temperature Polymers

### ABSTRACT

Aerogels were prepared so as to have a hybrid structure, by carrying out the supercritical drying process on composites consisting of an *in situ* generated silica network as the inorganic phase and a high-temperature polymer as the organic phase. The goal was to maintain the best properties of both components, for example, decreasing the brittleness of the ceramic phase by introducing a polymeric phase. A polybenzobisthiazole of very high thermal stability, with sulfonation to increase its reactivity, was chosen for the organic phase, and it was bonded to the silica phase by a silane coupling agent. A range of silica/polymer com-

---

\* Author to whom correspondence should be addressed. e-mail: markje@email.uc.edu,  
<http://jemcom.crs.uc.edu/>

positions were investigated, and the resulting materials were characterized in terms of their moduli and ultimate properties in compression. Increase in the amount of polymer present decreased the moduli but increased deformabilities, yielding relationships that should be useful in the design of aerogels of optimized properties. Values of Poisson's ratio were also determined and used to estimate longitudinal sound velocities, which can be important in some applications of aerogel materials in general.

## INTRODUCTION

Aerogels are a special class of materials with a highly porous structure. There are inorganic and organic aerogels as well as hybrid inorganic-organic aerogels of intermediate compositions. The unusual properties of aerogels such as extremely low thermal conductivity, slow sound propagation, and optical transparency recommend them for potential commercial applications, in spite of their unfortunate brittleness.

A number of years ago, aerogels were described as one of the top ten scientific and technological developments [1]. As their name implies, they are extremely porous materials, consisting more of air than gel [2, 3]. They are a special class of open-cell foams that have an ultrafine pore size ( $< 50$  nm), connected porosity, high surface areas ( $400\text{--}1000\text{ m}^2\text{ g}^{-1}$ ) and an ultrastructure composed of interconnected colloidal particles, or polymeric chains, with characteristic dimensions of 10 nm [4].

Because of their ultra-dispersed structures, aerogels have fascinating properties, including extremely low thermal conductivities ( $\sim 0.002\text{ W m}^{-1}\text{K}^{-1}$ ) [5, 6], unusual sound-propagation characteristics (sound velocities less than 100 m/s) [7], and unique optical properties. Recent applications include the development of thermal insulating windows [8], transparent thermal insulation for passive solar usage (e.g., to reduce the heating energy consumption of homes) [9], catalytic substrates with high surface areas [9], and detectors for Cerenkov radiation in high-energy particle physics [10]. Despite their highly unusual properties, there are some problems which impede aerogel commercial development, such as marked brittleness, limited transparency in some cases, and frequently a hygroscopic nature.

Traditionally, aerogels have been inorganic materials prepared by the sol-gel process [11, 12], which involves the hydrolysis and condensation of

metal alkoxides, e.g., tetraethoxysilane (TEOS)  $[\text{Si}(\text{OEt})_4]$ . It is also possible, however, to prepare novel aerogels from totally organic materials [13, 14] or from organic-ceramic hybrid materials [15-22]. In this sol-gel process, multifunctional monomers are cross linked into sol particles which then continue cross linking and, finally, form a continuous gel network. In order to preserve the gel structure from shrinking and cracking from the build-up of capillary forces during the drying process, super-critical drying is generally employed [15].

Recent studies have shown that the incorporation of small amounts of organic polymers into these fragile inorganic networks can dramatically increase their compression strength and toughness, improve their optical transparency, and decrease their hydrophilicity [15-22]. In the present investigation, some novel organic-inorganic hybrid aerogels are prepared. The organic component is a thermally-stable aromatic heterocyclic polymer, specifically a polybenzobisthiazole (PBT) which was sulfonated to increase its reactivity with a ceramic phase. The PBTs are rigid-rod polymers which are designed to maintain desirable properties at elevated temperatures [23]. They are being used for aerospace applications because of their exceptional weatherability and their resistance to hydrolytic attack and oxidation at elevated temperatures. The ceramic component will be a silica ( $\text{SiO}_2$ ) network in-situ generated using tetramethylorthosilicate (TMOS) by the sol-gel hydrolysis-condensation process [11]. Recent experimental results have shown that the use of a bonding agent can significantly improve the properties of such organic-ceramic composites [24-26]. In the present systems, chemical bridges between the organic and ceramic phases of the hybrid material will be formed from the bonding agent N,N-diethylamino-propyltrimethoxysilane. The polymer was a sulfobiphenylpolybenzobisthiazole (SBPPBT II) synthesized in the Wright-Patterson Air Force Laboratories specifically for this project [27] (Figure 1).

The mechanical behavior of silica aerogels is characteristic of brittle, perfectly elastic materials [28], but a number of studies have been conducted to

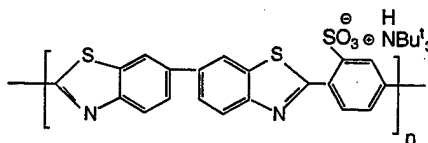


Figure 1. Structure of the SBPPBT II polymer.

investigate their elastic properties [29, 30]. The sound propagation characteristics for silica aerogels determined using both ultrasonic velocity measurements and mechanical property measurements have shown that they possess very low sound velocities [31-36]. It was hoped that introducing mechanically soft, elastic structures will make silica aerogels less brittle and promising acoustic materials, with applications in acoustic delay lines or high-temperature sound isolation [36]. The desirable low sound velocities in aerogels are due to low values of Young's modulus, which can be determined from compression measurements.

In the first part of this program, the goal was to produce novel aerogels from organic-ceramic hybrid materials, to study the effects of the amount of ceramic component present in the aerogel on compression strength, and sound velocity, and to provide guidance for the design of materials of optimized properties.

## EXPERIMENTAL

### Materials

The sample of SBPPBT II was prepared as described elsewhere [27], and the silane coupling agent was obtained from Huls America Inc. TMOS, tributylamine (99%), and methanol (99+%) were obtained from Aldrich.

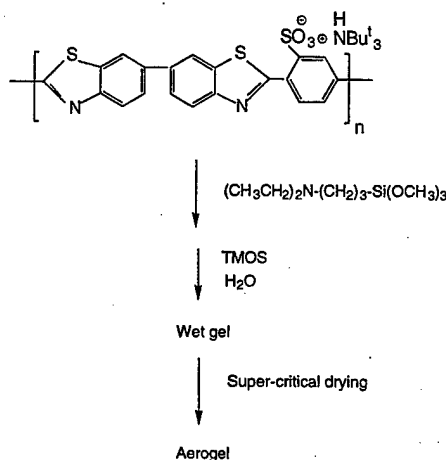
### Preparation of Aerogels

The SBPPBT II-SiO<sub>2</sub> aerogels were prepared according to Scheme 1.

Specifically, SBPPBT II, methanol, and tributylamine were placed into a three-neck flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet and outlet. The mixture was held at 50°C for 36 hours under a very slow stream of nitrogen. If some methanol escaped from the solution during refluxing, more was added to maintain an approximately constant amount. After a clear, homogeneous solution was obtained, it was cooled to room temperature and the silane coupling agent and TMOS were added. The mixture was stirred for another two hours at room temperature, and a stoichiometric amount of water was added to give a very viscous solution.

Stoichiometric amounts of the polymer and silane coupling agent, and varying amounts of TMOS were thus used to prepare a series of aerogel samples. The amounts of SiO<sub>2</sub> were varied by varying the amount of TMOS, and the amount of silica calculated included contributions from hydrolysis of the





**Scheme 1.** Preparation of SBPPBT II-silica aerogels.

trimethoxysilane groups on the coupling agent. The resulting solutions were placed into small cylindrical sample vials (5-cm heights, 2-cm diameters), subsequently giving gels having cylindrical shapes. After the vials were sealed, gelation was permitted to occur. The gels were removed from the vials and immersed in methanol, which was subsequently used as an exchange solvent for the drying. The methanol was exchanged by fresh methanol several times until no optical waves were observable upon stirring for four days. A solvent-exchange process was used to remove the water (which is immiscible with liquid  $\text{CO}_2$ ) from the pores of the gels. The gels were then placed into a E3000 critical point drying apparatus, and the methanol in the gels replaced by liquid  $\text{CO}_2$ , followed by supercritical drying at the critical point of  $\text{CO}_2$  (31.5 °C and 1100 Psi). This process prevents the delicate gel structure from the shrinking and cracking usually caused by the capillary forces formed in the cell pores in the case of non-critical solvent evaporation from the gel.

### Characterization Techniques

Bulk densities were determined from the weights and volume of the aerogel samples, and linear shrinkage extents by measurements of cylindrical sample diameters before and after the supercritical drying. Uniaxial compression was used to measure the moduli and ultimate strengths of the samples; uniaxial extension tests are not possible with materials too fragile for the required

clamping. These compression measurements were carried out at room temperature on an Instron testing machine, as a function of the amount of  $\text{SiO}_2$  present in the aerogel. The initial heights of the samples were approximately 1.5 cm, and they were compressed at a cross-head speed of 0.02 in/min. Values of the Poisson ratio  $\mu$  were determined from measurements of the sample dimensions before and after the compressions. Sound velocities were estimated from the stress-strain results.

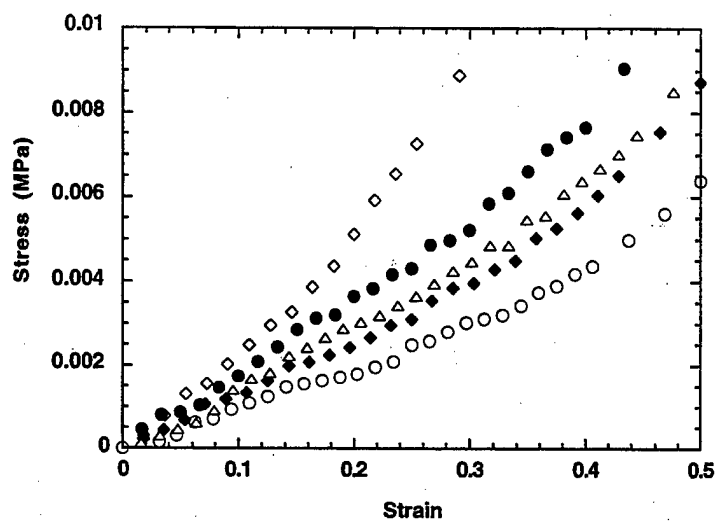
## RESULTS AND DISCUSSION

The SBPPBT II- $\text{SiO}_2$  aerogel samples prepared had the amounts of silica listed in the first column of Table 1. Columns two and three give values of the density and the relative linear shrinkage for the aerogels. The densities of the aerogels are seen to increase with increase in the amount of silica present, as expected, but the amount of shrinkage upon drying the gels did not vary in any significant way with the amount of silica present.

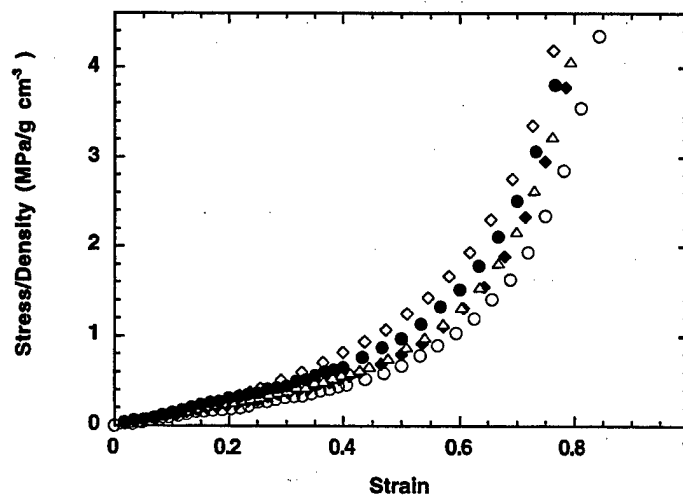
Figures 2 and 3 show the stress-strain results for the aerogels, where the strain is the relative change  $\Delta h/h$  in height of the sample, at the low or moderate deformations most important in their applications and at some high deformations, respectively. In Figure 3, the stresses have been normalized with values of the density, the ratio being important in applications in which the material is transported. Values of Young's modulus were obtained from the initial slopes of

TABLE 1. Densities and Linear Shrinkages for the Aerogels

$\text{SiO}_2$ :Polymer Weight Ratio	$10^3$ Density ( $\text{g/cm}^3$ )	$\Delta D/D$ (%)
12.5:100	9.58	13.4
22.5:100	11.0	11.1
32.5:100	11.3	12.3
42.5:100	11.8	14.6
62.5:100	17.5	13.4



**Figure 2.** Compressional stress-strain isotherms for SBPPBT II-SiO<sub>2</sub> aerogels: 12.5:100 (○), 22.5:100 (◆), 32.5:100 (△), 42.5:100 (●), and 62.5:100 (◇), SiO<sub>2</sub>:polymer weight ratio.



**Figure 3.** Compressional stress-strain isotherms in which the stress is normalized with the density; see legend to Figure 2.

the stress-strain isotherms (Figure 2). The polymeric phase introduced into these aerogels is seen to give these samples considerable deformability, i.e., significantly reduced brittleness.

Values of the longitudinal sound velocity for silica aerogels have been determined using the equation

$$c_1 = [Y(1 - \mu)/\rho(1 + \mu)(1 - 2\mu)]^{1/2} \quad (1)$$

where  $c_1$  is the longitudinal sound velocity (m/s),  $Y$  is the Young's modulus ( $\text{N m}^{-2}$ ),  $\mu$  is the Poisson's ratio, and  $\rho$  is the density ( $\text{g/l}$ ) [36]. Table 2 presents the values of  $Y$ ,  $\mu$ , and  $c_1$  of the resulting SBPPBT II-silica aerogels.

According to the literature, the maximum deformability of pure silica aerogels is very low ( $\sim 10\%$ ) [30], however, there are cases where the deformabilities of such *in situ* generated materials are as high as 60% [15, 37]. These increases in deformability may possibly be due to non-hydrolyzed groups remaining in the structure after the sol-gel process is terminated. In any case, the deformabilities of the SPBBPT II-SiO<sub>2</sub> aerogels have been significantly increased in comparison to the silica aerogels; i.e. incorporating this organic polymer into the aerogels did substantially increase their deformability. In addition, the increase in the amount of polymer in these aerogels decreases both the Young's modulus and the yield strength (Figure 2). These observations suggest that incorporation of organic polymer decreases the inherent brittleness of silica aerogels.

As the amount of silica was increased, Young's modulus increased, as expected, but the Poisson ratio did not show any obvious trend. Values of the lon-

TABLE 2. Young's Moduli, Poisson's Ratios, and Longitudinal Sound Velocities

SiO <sub>2</sub> :Polymer Weight Ratio	$10^3 Y$ ( $\text{N m}^{-2}$ )	$10^3 \mu$	$c_1$ (m/S)
12.5:100	9.74	3.82	31.8
22.5:100	12.3	1.50	33.4
32.5:100	14.2	3.14	35.4
42.5:100	17.5	0.99	38.5
62.5:100	22.3	1.02	35.7

gitudinal sound velocity did generally increase with increase in the amount of silica. In brief, the results suggest that introducing organic polymer into these aerogels decrease their brittleness, while maintaining relatively low values of the longitudinal sound velocity.

## CONCLUSION

Organic-inorganic aerogels were prepared using a high-temperature polymer and *in situ* generated silica. A range of silica/polymer compositions was investigated, and mechanical property measurements in compression indicated that increase in the amount of polymer present decreased the moduli but increased deformability. Thus, introducing the organic polymer into these aerogels was successful in reducing their brittleness.

## ACKNOWLEDGEMENT

It is a pleasure to acknowledge the financial support provided by the Air Force Office of Scientific Research (Directorate of Chemistry and Materials Science) through Grants F49620-96-1-0052 and -0235.

## REFERENCES

- [1] R. L. Guyer and D. E. Koshland, Jr., *Science*, **250**, 1642 (1990).
- [2] J. Gross, J. Lukas, J. Fricke, and F. Schwertfeger, in *Sol-Gel Processing and Applications*, Y. A. Attia, Ed., Plenum, New York, 1986.
- [3] *Proceedings, Fourth International Symposium on Aerogels*, R. W. Pekala and L. W. Hrubesh, Eds., Berkeley, CA, September, 1994.
- [4] G. E. Ruben, R. W. Pekala, T. M. Tillotson, and L. W. Hrubesh, *J. Mater. Sci.*, **27**, 4341 (1992).
- [5] J. Fricke, *J. Non-Cryst. Solids*, **100**, 169 (1988).
- [6] R. Caps and J. Fricke, *Sol. Energy*, **36**, 361 (1986).
- [7] M. Gronauer, A. Kadur, and J. Fricke, in *Aerogels*, J. Fricke, Ed., *Proc. in Phys.* **6**, Springer-Verlag, Berlin, 1986, p.167.
- [8] P. H. Tewari, A. J. Hunt, and K. D. Lofftus, *Mater. Lett.*, **3**, 363 (1985).

- [9] S. J. Teichner, *Chemtech*, June 1991, 372.
- [10] G. Poelz, in *Aerogels*, J. Fricke, Ed., Springer-Verlag, New York, 1986, p. 176.
- [11] C. J. Brinker and G. W. Scherer, *Sol-Gel Science*, Academic Press, New York, 1990.
- [12] *Better Ceramics Through Chemistry VII: Organic/Inorganic Hybrid Materials*, B. K. Coltrain, C. Sanchez, D. W. Schaefer, and G. L. Wilkes, Eds., Materials Research Society, Warrendale, PA, 1996.
- [13] R. W. Pekala, C. T. Alviso, and J. D. Lemay, in *Chemical Processing of Advanced Materials*, L. L. Hench and J. K. West, Eds., John Wiley & Sons, Inc., New York, 1992, p. 671.
- [14] J. Gross, G. W. Scherer, C. T. Alviso, and R. W. Pekala, *J. Non-Cryst. Solids*, **211**, 132 (1997).
- [15] B. M. Novak, D. Auerbach, and C. Verrier, *Chem. Mater.*, **6**, 282 (1994).
- [16] F. Schwertfeger, W. Glaubitt, and U. Schubert, *J. Non-Cryst. Solids*, **145**, 85 (1992).
- [17] U. Schubert, F. Schwertfeger, N. Husing, and E. Seyfried, in *Better Ceramics Through Chemistry VI*, A. K. Cheetham, C. J. Brinker, M. L. Mecartney and C. Sanchez, Eds., Materials Research Society, Warrendale, PA, 1994, Vol. 346, p. 151.
- [18] F. Schwertfeger, A. Emmerling, A. J. Gross, U. Schubert, and J. Fricke, in *Sol-Gel Processing and Applications*, Y. A. Attia, Ed., Plenum Press, New York, 1994, p. 185.
- [19] N. Husing, F. Schwertfeger, W. Tappert, and U. Schubert, *J. Non-Cryst. Solids*, **186**, 37 (1995).
- [20] F. Schwertfeger and U. Schubert, *Chem. Mater.*, **7**, 1909 (1995).
- [21] J. Kuhn, F. Schwertfeger, M. C. Arduini-Schuster, J. Fricke, and U. Schubert, *J. Non-Cryst. Solids*, **186**, 184 (1995).
- [22] N. Husing, U. Schubert, B. Riegel, and W. Kiefer, in *Better Ceramics Through Chemistry VII: Organic/Inorganic Hybrid Materials*, B. K. Coltrain, C. Sanchez, D. W. Schaefer, and G. L. Wilkes, Eds., Materials Research Society, Warrendale, PA, 1996, p. 339.
- [23] P. E. Cassidy, *Thermally Stable Polymers*, Marcel Dekker, New York, 1980.

- [24] J. P. Chen, Z. Ahmad, S. Wang, J. E. Mark, and F. E. Arnold, in *Hybrid Organic-Inorganic Composites*, J. E. Mark, P. A. Bianconi, and Y-C. Lee, Eds., American Chemical Society, Washington, 1994, 297.
- [25] J. Premachandra, C. Kumudinie, W. Zhao, W., J. E. Mark, T. D. Dang, J. P. Chen, and F. E. Arnold, *J. Sol-Gel Sci. Technol.*, **7**, 163 (1996).
- [26] J. E. Mark, J. Premachandra, C. Kumudinie, W. Zhao, T. D. Dang, J. P. Chen, and F. E. Arnold, in *Better Ceramics Through Chemistry VII: Organic/Inorganic Hybrid Materials*, B. K. Coltrain, C. Sanchez, D. W. Schaefer, and G. L. Wilkes, Eds., Materials Research Society, Warrendale, PA, 1996, p. 93.
- [27] T. D. Dang, J. P. Chen, and F. E. Arnold, in *Hybrid Organic-Inorganic Composites*, J. E. Mark, P. A. Bianconi, and Y-C. Lee, Eds., American Chemical Society, Washington, 1994, p. 280.
- [28] T. Woignier and J. Phalippou, *J. Non-Cryst. Solids*, **100**, 404 (1988).
- [29] J. Gross and J. Fricke, *J. Non-Cryst. Solids*, **145**, 217 (1992).
- [30] K. E. Parmenter and F. Milstein, *J. Non-Cryst. Solids*, **223**, 179 (1998).
- [31] J. Gross and J. Fricke, *J. Non-Cryst. Solids*, **146**, 217 (1992).
- [32] J. Gross, T. Schlieff, and J. Fricke, *Mat. Sci. Eng.*, **A168**, 235 (1993).
- [33] R. Gerlach, O. Kraus, and J. Fricke, *J. Non-Cryst. Solids*, **145**, 227 (1992).
- [34] E. Courtens, J. Pelous, J. Phalippou, R. Vacher and T. Woignier, *Phys. Rev. Lett.*, **58**, 128 (1987).
- [35] J. D. Lemay, *Mat. Res. Symp. Proc.*, **207**, 21 (1991).
- [36] M. Gronauer and J. Fricke, *Acustica*, **9**, 177 (1986).
- [37] J. K. Premachandra, C. Kumudinie, J. E. Mark, T. D. Dang, and F. E. Arnold, unpublished results.

Received March 30, 1998

Revision received August 20, 1998